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Effect of Electrolyte Concentration, Temperature and Clay Type on the Diffusional Properties of Anions in Clay-Modified Electrodes

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EFFECT OF ELECTROLYTE CONCENTRATION, TEMPERATURE AND CLAY TYPE ON THE DIFFUSIONAL PROPERTIES OF ANIONS IN CLAY-MODIFIED ELECTRODES

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LIST OF PUBLICATIONS

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LIST OF ABBREVIATIONS

CEC	Cation Exchange Capacity
CME	Clay-modified Electrode
CV	Cyclic Voltammogram
DAC	Digital-to-Analog Convertor
DLVO	Derjaguin, Landau, Verwey, and Overbeek
EE	Edge-to-Edge Structure
EF	Edge-to-Face Structure
FF	Face-to-Face Structure
I_{pbare}	Peak Cathodic Current for Bare Electrode
I_{pc}	Peak Cathodic Current
I_{pcme}	Peak Cathodic Current for Clay-modified Electrode
KGa-1	Kaolinte, Georgia, Well Crystallized
Oh	Octahedral Geometric Configuration
SAz-1	Smectite, Arizona Montmorillonite
SCE	Saturated Calomel Electrode
SFA	Surface Force Apparatus
SHCa-1	Smectite, California Hectorite
SPCME	Spin Coated Clay-modified Electrode

STx-1	Smectite, Texas Montmorillonite
SWy-1	Smectite, Wyoming Montmorillonite
Td	Tetrahedral Geometric Configuration

CHAPTER 1

INTRODUCTION

I. Statement of the Problem

The goals of this project are twofold. The first goal is to design an instrumental control system for use in clay-modified electrode studies. The second goal is to use this system to study the effect of electrolyte concentration, clay type and temperature on the diffusional properties of clays.

The diffusional properties of clays control the transport of pollutants through clay beds which underlay waste disposal sites. Both the types of clays present and the level of hydration of these clays affect these properties. When a clay bed is composed of a variety of clays, each clay will interact differently with the diffusing pollutant.[1,2]

Dehydration of a clay bed can cause large fissures to form. These fissures allow ready transport of pollutants.[3] In a hydrated clay bed pollutants are able to diffuse through the region between the clay layers.[4,5,6,7] All of these phenomena can be studied with clay-modified electrodes. Additionally, the study of clay-modified electrodes can provide insights into the fundamental physical chemistry of the clay.

The shrinking and swelling of the clay's interlayer region has been studied by a variety of disciplines. This is due to the effect clay swelling has on the stability of landfills, the stability of structures built on clayey soils, and the use of clays in drilling fluids. Despite this intensive study, the exact nature of this phenomena is still not fully

understood. Clay-modified electrodes can provide an easy and accurate method for further studying these processes.

II. Clay Chemistry Background

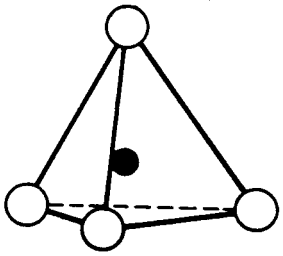
II.1. Clay Structure

II.1.1 General Structure

Clays belong to the phyllosilicate family of minerals.[8] The clay structure is composed of two-dimensional layers.[9] These layers are composed of sheets with two basic geometric configurations. The tetrahedral configuration (Td) consists of silica atoms coordinated in tetrahedral symmetry with four oxygen atoms (Figure 1A). The other primary layer configuration is termed the octahedral layer (Oh). It consists of aluminum or magnesium atoms coordinated in octahedral symmetry with oxygen atoms and hydroxyl groups (Figure 1B). If alumina is present as the octahedral cation, every third cation center is vacant and the octahedral sheet is termed dioctahedral. If magnesium is present, all octahedral cation positions must be occupied in order to maintain charge neutrality, and the octahedral sheet is termed trioctahedral.[10] The Oh and Td sheets join together through shared oxygen atoms to form the layers of a clay.

The sharing of the negatively charged oxygen atoms is a driving force in the formation of clay layers. Another factor that drives this formation is simply the similar geometry of the two layers.[11] The separation between the oxygen atoms in the tetrahedral and the octahedral sheets correlates to within 3 to 5% of the ideal sheet

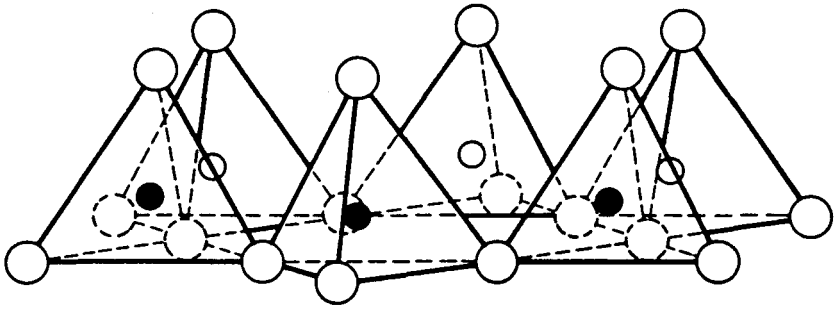
Figure 1: A) Structure of tetrahedral layer configuration and of B) octahedral layer configuration. In the figures (a) represents a single sheet unit, (b) represents a sheet structure. (Reprinted with permission from Grim.[9])



(a)

○ and ◌ = Oxygens

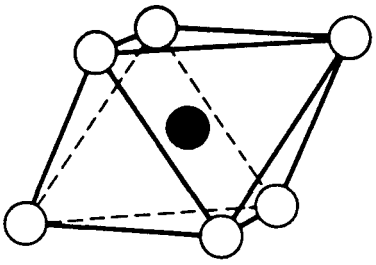
○ and ● = Silicons



(b)

A

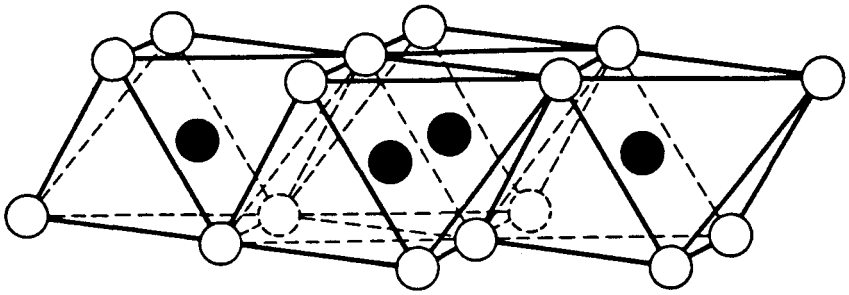
B



(a)

○ and ◌ = Hydroxyls

● Aluminums, magnesiums, etc.



(b)

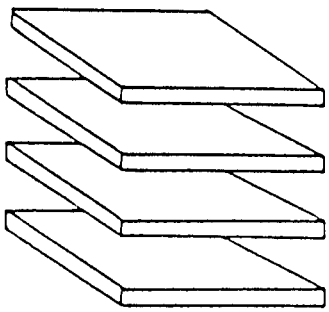
structure based on theoretical calculations.[10] As a result, these sheets are easily able to merge.

Due to the parallel alignment of the sheets in the clay layers, clays have two surfaces. The long flat surface that is composed of the plane of the layers is termed the face. The area where the layers end is termed the edge. In this area, the components of the clay layer are exposed. While the charge on the edge is pH dependent, in most situations, the edge is considered to have a positive charge.[11] The face of the clay layer has a negative charge. This is due to random substitutions, termed isomorphous substitutions within the clay layer. These substitutions are of cations with similar size but lower charge for the primary layer cations. The negative charge of the clay is compensated by exchangeable cations which are associated with the surface of the clay.

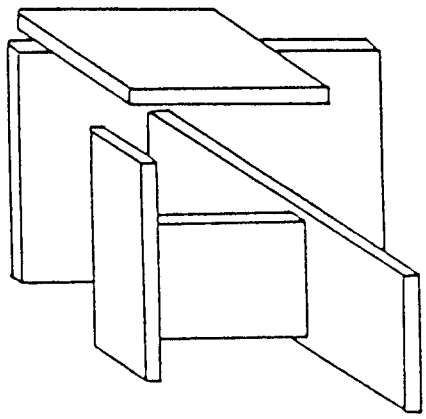
Clay layers can align in either an edge-to-face (EF), an edge-to-edge (EE), or a face-to-face (FF) arrangement[11] (Figure 2). In the EF and EE arrangements, a bulky structure termed the house of cards structure is formed. This structure arises from the interaction of the negatively charged clay faces with the positively charged edges. In the FF structure, the faces align in a parallel manner. It is this structure that is formed when a clay is dried.[12] The region between the clay layers in the FF structure is termed the interlayer region. It is this interlayer region that controls many of the properties of a clay film.

Three parameters of clays which are commonly measured are the cation exchange capacity (CEC), the surface area, and the surface charge density. The CEC measures the amount of exchangeable cations present in the clay. This measurement correlates to

Figure 2: Examples of A) face-to-face and B) edge-to-face arrangements of clay sheets. (Reprinted with permission from Lee and Fitch.[13])



A



B

the magnitude of the isomorphous substitutions in the clay layers and to the charge on the edge of the clay. The surface area of a clay is also important. It is a measure of the roughness of the clay surface. The surface charge density of a clay is derived from the CEC and surface area. It measures the area on the clay which a single charge occupies.

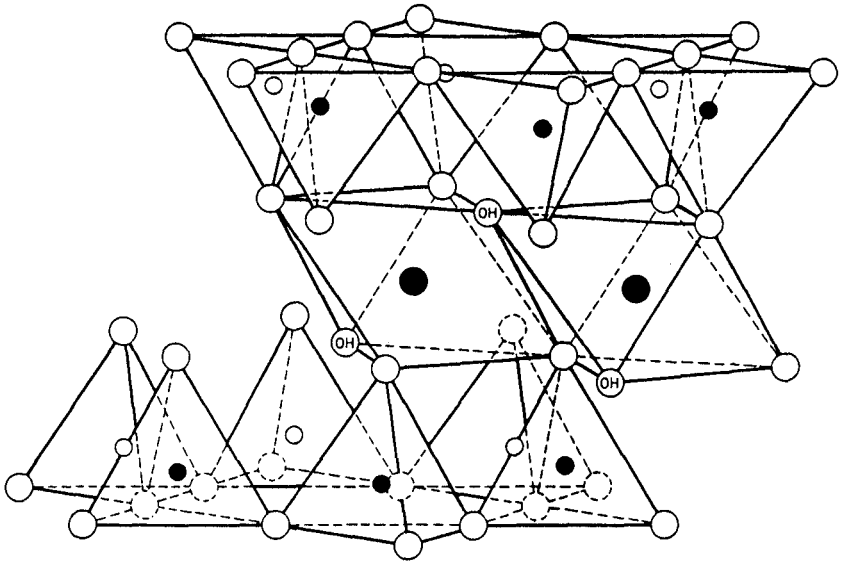
II.1.2. 2:1 Layer Clays

In the arrangement of clay layers termed 2:1, an Oh layer is sandwiched between two Td layers (Figure 3). In this arrangement, the interlayer region of the clay is bounded by planes of oxygen from the two Td layers. This results in minimal attraction between the adjacent layers. The 2:1 layer clays generally have a large degree of isomorphorous substitution and thus, the cation exchange capacity in these clays is large. It is estimated that eighty percent of the cations within the clays reside between the clay sheets in the interlayer region.[8, 9]

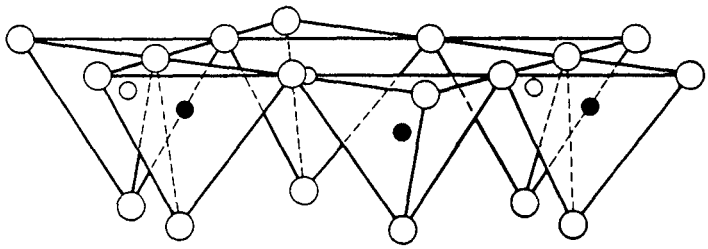
II.1.3. 1:1 Layer Clays

In the arrangement of sheets termed 1:1, there is one Td sheet for each Oh sheet (Figure 4). In the 1:1 arrangement, the clay interlayer is bounded by a sheet of oxygens from the Td layer and a sheet of hydroxyls from the Oh layer. Hydrogen bonding between these two layers results in a strong attraction between the layers. The 1:1 clays have a low degree of isomorphous substitution and thus, a low cation exchange capacity.[8, 9]

Figure 3: Structure of montmorillonite, a 2:1 dioctahedral clay. (Reprinted with permission from Grim.[9])



Exchangeable cations
nH_2O

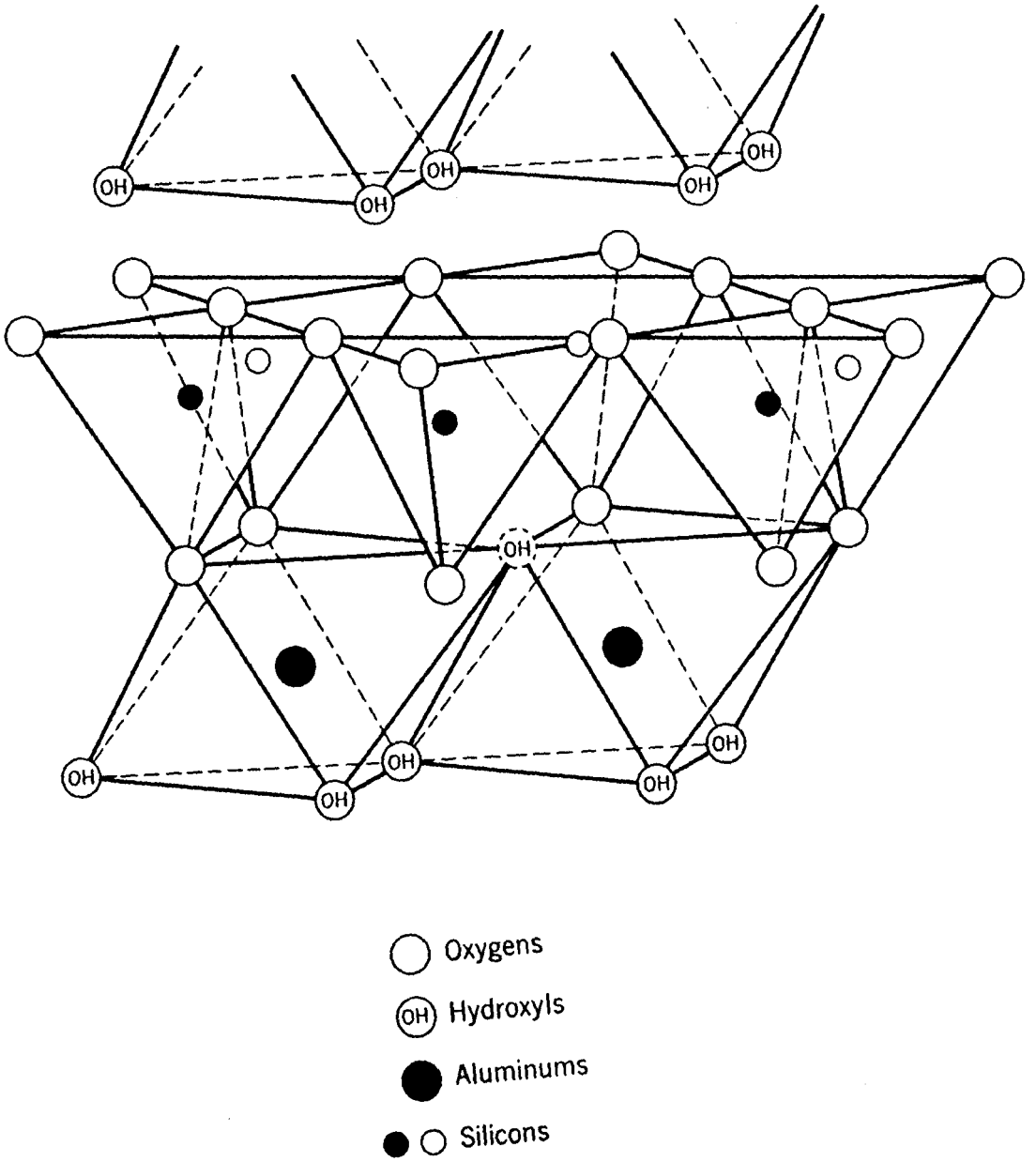


○ Oxygens (OH) Hydroxyls

● Aluminum, iron, magnesium

○ and ● Silicon, occasionally aluminum

Figure 4: Structure of kaolinite, a 1:1 layer clay. (Reprinted with permission from Grim.[9])


OH
OH
OH
OH
OH
OH
OH
OH
OH
OH
OH
OH
Oxygens
Hydroxyls
Aluminums
Silicons

II.2. Clay Swelling

II.2.1. Methods Used to Study Clay Swelling

Since the swelling of clays is important in a variety of applications, different disciplines have studied the process. As a result, many different methods have been used to study both the swelling of clays and the factors that affect this phenomena.

Methods used to study clay swelling can be categorized into either direct or indirect observations. Direct observation of clay swelling is most often done with X-ray diffraction.[14,15,16,17,18,19,20] This method measures the interlayer spacing of the clay at equilibrium in response to some controlled condition. A different sample must be prepared for each condition that is to be studied. Sample preparation and analysis are both time consuming and the equipment for this analysis is quite costly. The method does, however, directly measure the interlayer spacing in the clay film and indicate the degree of randomness present within the film. Neutron diffraction[21] and synchrotron X-ray diffraction have also been used to directly study the interlayer spacing in the clay film. These methods give the same information as X-ray diffraction but they are able to measure smaller spacings with greater resolution.

Scanning electron microscopy has been used to directly examine the structure of the clay films.[22,23] It does not yield information on the interlayer spacing of the clay film but it does give important information on the overall organization of the clay structure.

In the late 1970s, the surface force apparatus (SFA) was developed to directly measure the forces present between two planar surfaces when immersed in a liquid.[24] In this instance, the interlayer spacing is controlled by the apparatus and the forces in changing from one spacing to another are measured. The apparatus is most often used to examine the forces present between two mica sheets when they are pushed together.[25,26,27,28,29,30,31] While these are idealized studies, and they actually examine the shrinking rather then the swelling of a planar film, they have provided vital insight into the forces that are present in clay films.

Indirect measurements of the swelling of a clay film are used to examine certain properties of a clay film. A standard method used to determine the swelling of the clay film is measurement of the weight of water that a clay film has adsorbed.[32,33,34,35,36] This method is easy and it allows for a single sample to be examined at different conditions. It does not, however, follow the kinetics of the changes from state to state.

Methods used to measure properties that can then be related to the interlayer spacing are commonly used. These include optical methods including IR,[37] NMR, and light scattering.[38] These methods directly measure a property, such as the structure of water in the interlayer. This property is then related to the swelling of the clay film. Measurements of the rheology of a clay solution include measurements of the viscosity,[39] shear stress,[40,41] and settling rate.[22] These measurements yield information on the particle to particle interactions present in a clay. While this doesn't apply directly to swelling, swelling affects these interactions and, hence, the measurements correlate to swelling.

Studies on the diffusion of a species through a clay can determine the interlayer spacing in the clay film. They can also measure the void space in a clay, which in turn is related to the particle alignment in the clay, which is then related to the swelling of the clay. The most common method to study this phenomena is column diffusion.[2,5,6,23,42,43] This method is used by soil scientists who are implicitly concerned with the diffusional properties of a clay. Both clay swelling and particle to particle interactions affect this measurement. Another example of this type of study is a rainfall simulator[44] which directly studies the affect of rain on the structure of soils. These methods are very slow but, as indicated, they directly measure the diffusional properties of the clay.

In our laboratory, we measure the diffusion of species through the clay film with clay-modified electrodes. Depending on the conditions, these studies yield information on the interlayer spacing in the clay film or on the arrangement of particles in the clay film. CME studies are quick, dynamic, and can follow a single clay film through a series of conditions.

II.2.2 Factors that Effect Clay Swelling

The primary factors that affect clay swelling are the clay type, the degree of isomorphous substitutions within the clay layers, the location of these substitutions, and the types of exchangeable cations present. Environmental factors that affect clay swelling are the liquid it is exposed to, prior treatment, and temperature.

In general, the 2:1 layer clays swell while the 1:1 layer clays do not. The absence of cations and the presence of hydrogen bonding between the clay layers causes

the 1:1 layer clays to not swell in water and salt solutions. Alternatively, the low attraction between the layers and the presence of interlayer cations causes the 2:1 layer clays to swell or expand their interlayer region in water and in dilute salt solutions.

Within the 2:1 layer clay family there are differences in the swelling response. One cause for these differences is the arrangement of cations in the octahedral layer. In the Oh layer there is a net negative charge of -6 from the oxygens and hydroxyl groups that must be balanced by the cations within the lattice. In a dioctahedral clay, this charge is balanced by two Al^{3+} atoms. In a trioctahedral clay, the charge is balanced by three Mg^{2+} atoms. In general, a trioctahedral clay will swell more readily then a dioctahedral clay.[19]

The location, type, and degree of isomorphous substitutions in the clay structure also need to be considered. In general, isomorphous substitutions increase the surface charge on the clay, increase the CEC of the clay, and change the geometry of the sheets in which the substitutions occur. Neither surface charge nor CEC relate directly to the swelling characteristics of the clay.[45] In both these instances, there appears to be a gradual increase in swelling, then a decrease. The location of the substitution relates directly to swelling. Substitutions in the Oh layer appear to affect swelling to a larger degree then those in the Td layer.[19] This could be due to the observation that substitutions in the Oh layer distort the geometry of the clay layer to a greater degree. In general, distortions in the geometry of the clay tend to lower swelling.[24]

Experimentally, the type of exchangeable cation has been found to affect clay swelling. The effect can be correlated to either ion size[17,46,47] or to the hydration energy

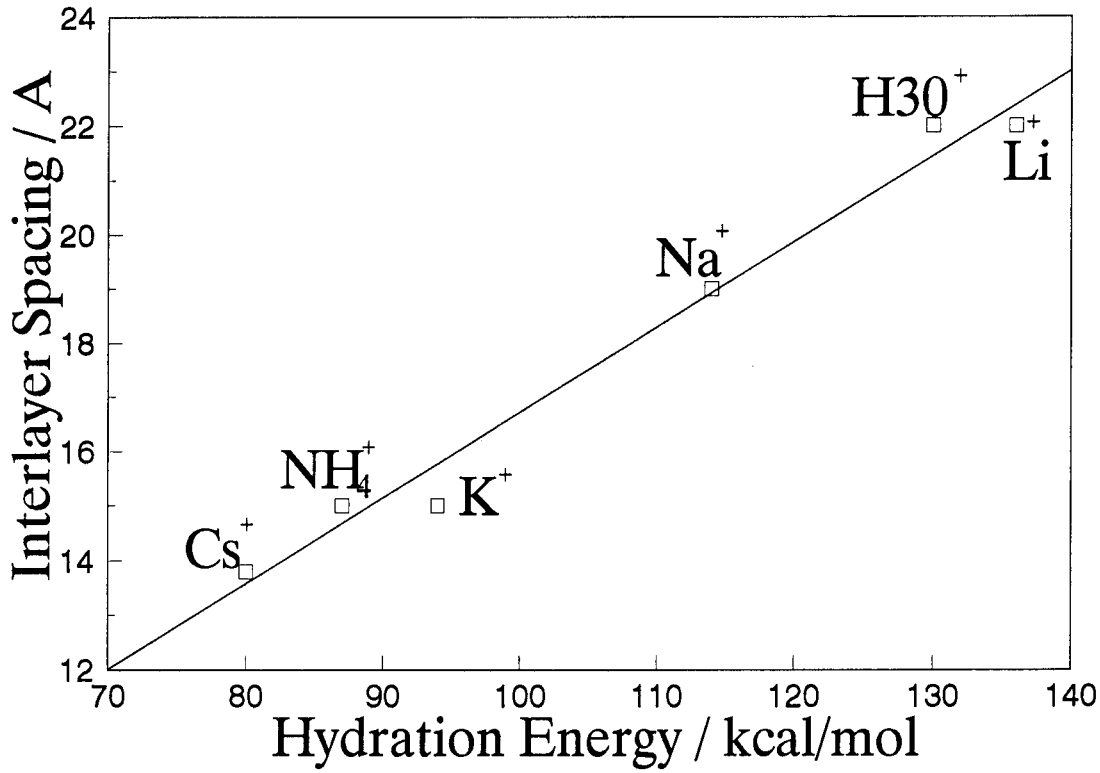
of the cation[14,16,28] (Figure 5). The smaller the ion, or the greater the hydration energy, the less the clay swells.

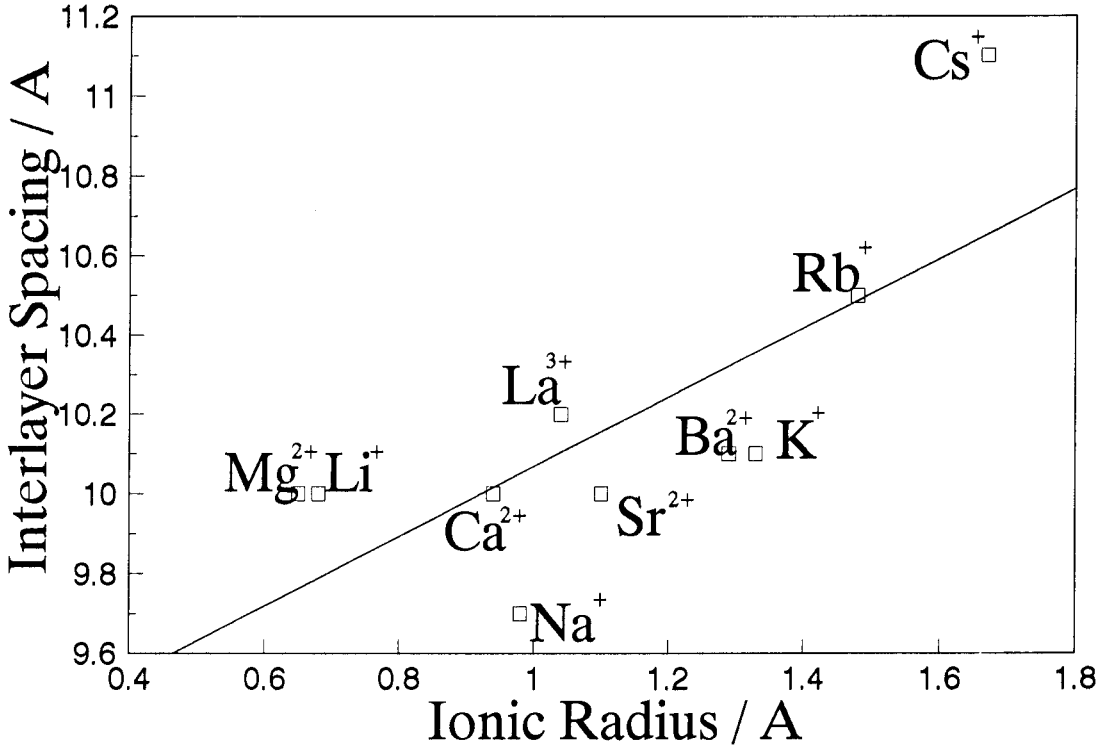
Environmental factors that affect swelling are the type of liquid, the salt concentration and type of salt present in the liquid, prior handling of the clay, and temperature. While clay swelling is not restricted to water, the majority of studies, including the present, focus exclusively on swelling in water. As with the exchangeable cations, there is a correlation between the hydration energy of the salt present in the system and the degree of swelling. Salt concentration also effects swelling. The higher the salt concentration, the less the clay will swell (see Section IV.1). Hysterisis in terms of both interlayer expansion and compression exist.[14,27,28,47] Temperature has the obvious effect on diffusion through the clay film. It does not, however, appear to correlate to the interlayer expansion of the film.[35] Any theory of clay swelling needs to address all of these observed dependencies.

II.2.3. Theory and Experimental Studies of Clay Swelling

Traditionally, clay swelling has been modeled by Derjaguin, Landau, Verwey and Overbeek (DLVO) theory. According to this theory, the interlayer spacing in a clay film is the spacing at which the attractive van der Waals forces are balanced by the repulsive electrostatic or double layer forces.[48] The repulsive double layer forces are modeled by the Stern-Guoy model.[49] In this model, the surface charge density of the clay and the exchangeable cations are the most important parameters in determining the clay's swelling.

Figure 5: Correlation of clay swelling with A) hydration energy of exchangeable cation and B) ion size. (Data in A) from Norrish, Table 2,[15] B) Adapted from Del Pennino, et al, Table 1.[17])


Interlayer Spacing / A
Hydration Energy / kcal/mol
H30+
Li+
Na+
NH4+
K+
Cs+
24
22
20
18
16
14
12
70
80
90
100
110
120
130
140


Interlayer Spacing / A
Ionic Radius / A
Cs+
Rb+
La3+
Ba2+
K+
Mg2+
Li+
Ca2+
Sr2+
Na+
11.2
11
10.8
10.6
10.4
10.2
10
9.8
9.6
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8

When the clay is placed into water or an electrolyte solution, the negative charge on the clay sheets causes an excess of positive charge to develop near the surface of the clay (Figure 6). The first layer of this excess charge is termed the Stern layer. It consists of a single layer of molecules associated with the clay surface. The Guoy layer is a diffuse layer of cations which extends from the surface of the Stern layer into solution (Figure 7). The thickness of this layer is described by double layer theory.

Double layer theory combines a series of equations to arrive at the thickness of the diffuse double layer on a charged surface. In essence, the counter-ions in the double layer are subject to two opposing forces. Electrostatic forces drive them towards the oppositely charged surface while diffusion drives them away from the surface towards solution equilibrium. Ions with the same charge as the surface are subject to the opposite forces. The balance of these two forces is described by Boltzmann's theorem:

$$C_i = C_i^* \exp(z_i F\Phi/RT) \qquad [1]$$

in which C_i is the local concentration of ions with charge i, C_i^* is the concentration of ions far from the surface in the unperturbed bulk solution, z_i is the valence of the ion, F is Faraday's constant (F = 9.6484.6 C mol^{-1}), Φ is the potential at the point in solution under study, R is the natural gas constant (R = 8.3144 J mol^{-1} K^{-1}), and T is the absolute temperature in Kelvin.

The density of charge and the electric potential in this area are described by the Poisson equation:

$$d^2\Phi/dx^2 = -\rho/\epsilon\epsilon_o \qquad [2]$$

Figure 6: Graphic depiction of anion and cation concentrations near a clay surface. A) is in a low electrolyte concentration while B) is in a high concentration electrolyte.

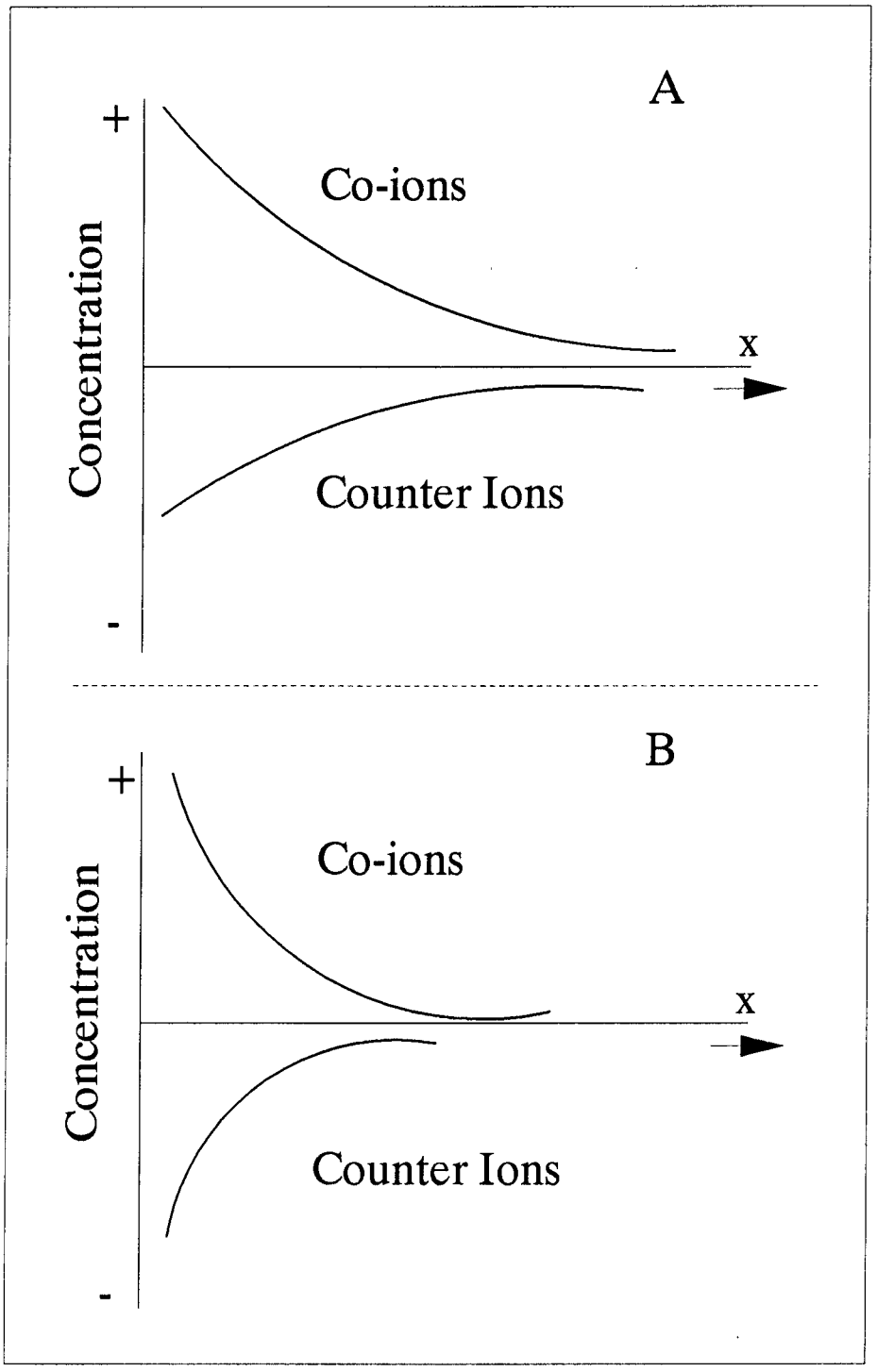
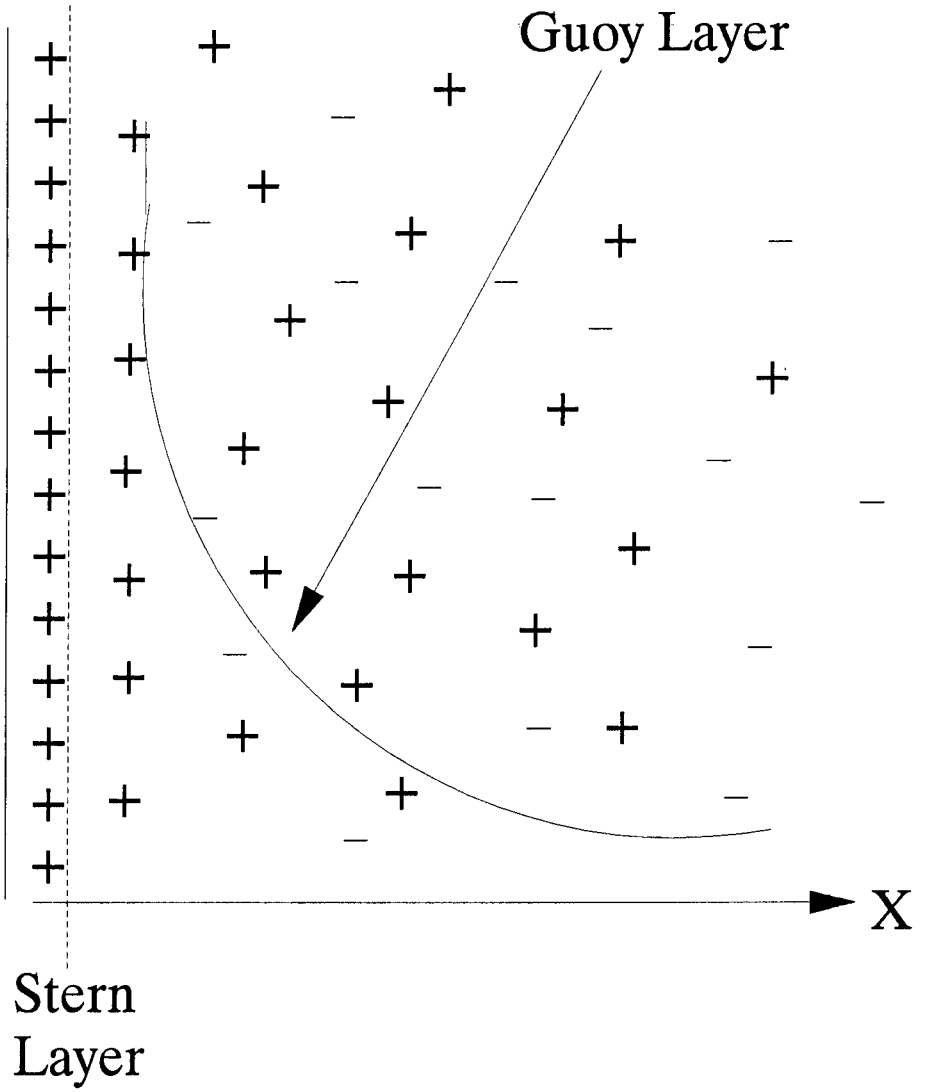

A
+
Concentration
Co-ions
x
Counter Ions
-
B
+
Concentration
Co-ions
x
Counter Ions
-

Figure 7: Model of the distribution of the diffuse double layer near a negatively charged clay surface. (Adapted from van Olphen.[11])


Guoy Layer
X
Stern
Layer

in which $d^2\Phi/dx^2$ is the variation in the electric field potential with distance, x, ρ is the space charge density, ϵ is the dielectric constant of the medium, and ϵ_o is the permittivity of a vacuum ($\epsilon_o = 8.854 \times 10^{-12}$ C^2 J^{-1} m^{-1}).

The space charge density is a function of the concentration and valence of the ions in the solution:

$$\rho = \Sigma z_i F C_i \qquad [3]$$

where all parameters are as previously defined.

Combining equations [1], [2], and [3], results in the fundamental equation of diffuse double layer theory, the Poisson-Boltzmann equation:

$$d^2\Phi/dx^2 = F/\epsilon\epsilon_o \, \Sigma z_i C_i^* \exp(z_i F\Phi/RT) \qquad [4]$$

where all parameters are as previously defined. In essence, this equation describes the thickness of the perturbation caused by the charged clay surface. The equation indicates that as the concentration of electrolyte, or cation, increases, the thickness of the diffuse Guoy layer decreases.

DLVO theory combines the diffuse double layer repulsive forces with attractive van der Waals forces to arrive at the interlayer spacing. DLVO theory accurately describes the long range swelling of a clay film. It does not, however, accurately predict the initial swelling of the clay film[24] or the lack of swelling in calcium clays.[50,51] Neither the role of water in the clay interlayer nor the position of the cations in the interlayer are addressed in DLVO theory. While the original research expressed concerns about these

omissions,[14,15] recent literature has shown that these considerations are vital to an analysis of clay swelling.

Measurements of the forces present in the interlayer indicate that hydration forces are crucial in the swelling of the clay.[24] The origin of the hydration force is not entirely clear. It could be either the hydration of the cations in the midplane of the interlayer, the hydration of the cations on the clay surface, the hydration of the clay surface, or the interaction of the water with itself.

DLVO theory assumes that it is the hydration of the cations that drives clay swelling. If the cations are located midway between the clay sheets, the water molecules will form their hydration shells around the cation, hydrogen bond to one another, and to the silicate surface.[17,51] Alternatively, the cations could also be located near the surface of the clay[11, 40] either on top of the surface or imbedded in the ditrigonal silane cavities. In these instances, the cations affect the structure of the water on the clay surface and thus, effect the swelling of the clay.[27,52] All of these theories address the observed correlation between the hydration energy of the exchangeable cation and the degree of clay swelling.

Another theory is that the surface of the clay is the primary factor in determining swelling.[17,18] In this theory, the water bonds to the surface of the clay to form a primary layer[11, 40] and this layer serves as a template for further water structure.[45] This theory explains the experimental evidence that indicates no correlation between CEC or surface charge density and clay swelling but does indicate a correlation with the location of the isomorphous substitution. Isomorphous substitutions affect the geometry within the clay

layer which, in turn, affects the geometry of the original water layer, and thus, all subsequent layers.[45] Additionally, experimental observations of the alignment of the clay layers indicate that skewing of the clay layers results in lower swelling.[31] The observed correlations with cation hydration energy are explained by stating that the cations are adsorbed to the clay surface and, thus, affect the clay structure.[52] Support for this theory comes from electrophoretic measurements that place the location of the cation next to the clay surface rather then in the midplane of the interlayer.[34]

In recent years, the surface force apparatus (SFA) has been used to directly measure the forces present in the clay interlayer. These results indicate that both hydration of the surface and hydration of the cation play a role in the swelling of the clay.[27,28] Based on these results, none of the above theories can be entirely true.

Another factor to be considered in clay swelling is the homogeneity of the clay structure. As indicated, the location of the isomorphous substitutions is important. Additionally, the overall distribution of the substitutions is important. Experiments with reduced iron clays[20] indicate that if the clay is not homogeneously charged, the clay will not evenly swell. In other words, domains can develop in the clay layer where different degrees of swelling occur. Other experiments that support the presence of domains are studies done with ion-exchanged clays.[32] If less then fifty percent of the calcium in a calcium clay is exchanged for sodium, the clay does not swell. The response of the entire clay is controlled by the calcium domains. At greater then fifty percent exchanged sodium, the clay behaves as a mixture of the two systems. As the percentage of sodium increases, so does the "sodium-like" swelling behavior.

In addition to the homogeneity of the clay, the overall structure of the clay platelets need to be considered in swelling. When the clay is in its dry state the clay platelets are in a collapsed turbostatic state.[37,52] This means that while they are aligned parallel to one another, in a face-to-face configuration, there is random rotation around the z or stack axis. As the clay swells, water enters the interlayer region between the clay platelets and the layers are able to rearrange and expand. Rearrangement of the platelets occurs relative to one another in order to best accommodate the interlayer water molecules. This results in rotation around the z axis. When water is removed from the system the platelets collapse but they do not rearrange. This results in a structure that is not the same as the original structure. It is this rearrangement of the clay layers which has been used to explain the phenomena of hysterisis within the clay film.

In summary, the following picture of clay swelling can be presented: When a dry clay film is placed in water the water penetrates the interlayer. The water interacts with the clay structure either due to the clay surface or due to the cations associated with it and a single water layer forms. This water layer serves as a template for the next water layer and layers of water form in the interlayer. This results in an increase in the interlayer spacing. After 4 layers of water have penetrated the interlayer in this manner, the clay enters the region of long range swelling and DLVO theory takes over. This picture of clay swelling has been substantiated by both direct and indirect measurements. It explains the observed dependence of swelling on clay type, exchangeable cation, and electrolyte concentration.

IV. Electrochemical Clay Studies

IV.1. Technique : Cyclic Voltammetry

In our laboratory, clay-modified electrodes are used to examine the diffusional properties of clay films. The technique used for this measurement is cyclic voltammetry. The general reaction observed by this method is:

$$O + e^- \rightleftarrows R \qquad [5]$$

where O is the oxidized form of the species, R is the reduced form of the species and e^- is an electron.

In a cyclic voltammetric experiment, the potential of the electrode is changed linearly with time (Figure 8).[53] The flux generated by the diffusion of an electroactive probe to the electrode surface in response to this changing potential is measured. The scanning of potentials is begun positive of the potential where an electrode reaction will occur. As the potential is scanned negative, a current will develop from the reduction of the probe. As the negative potential increases, this current will decrease due to depletion of the species in the diffusion layer. When the direction of the scan is changed there is a build up of the reduced probe in the diffusion layer. As the potential is scanned positive, this species is oxidized, then depleted (Figure 9).

The governing equation for a cyclic voltammetric experiment is the Randles-Sevcik expression:[54]

$$i_p = (2.69 \times 10^{-5})n^{3/2}AD_s^{1/2}\nu^{1/2}C^* \qquad [6]$$

Figure 8: Example of a typical excitation signal used in cyclic voltammetry. Switching potentials are 0.8 and -0.2 V vs SCE. (Adapted from Sawyer, Heineman, and Beebe.[53])

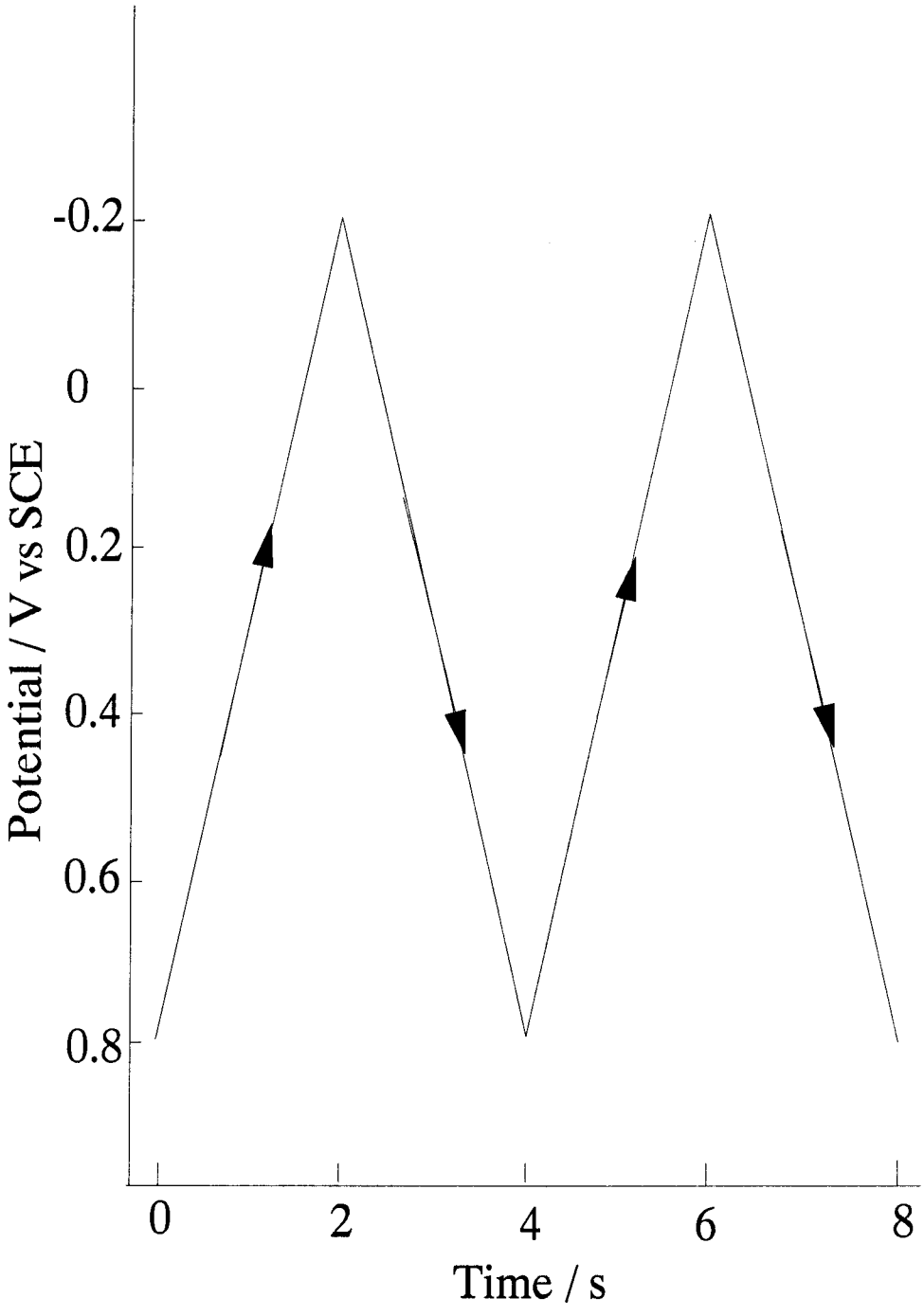
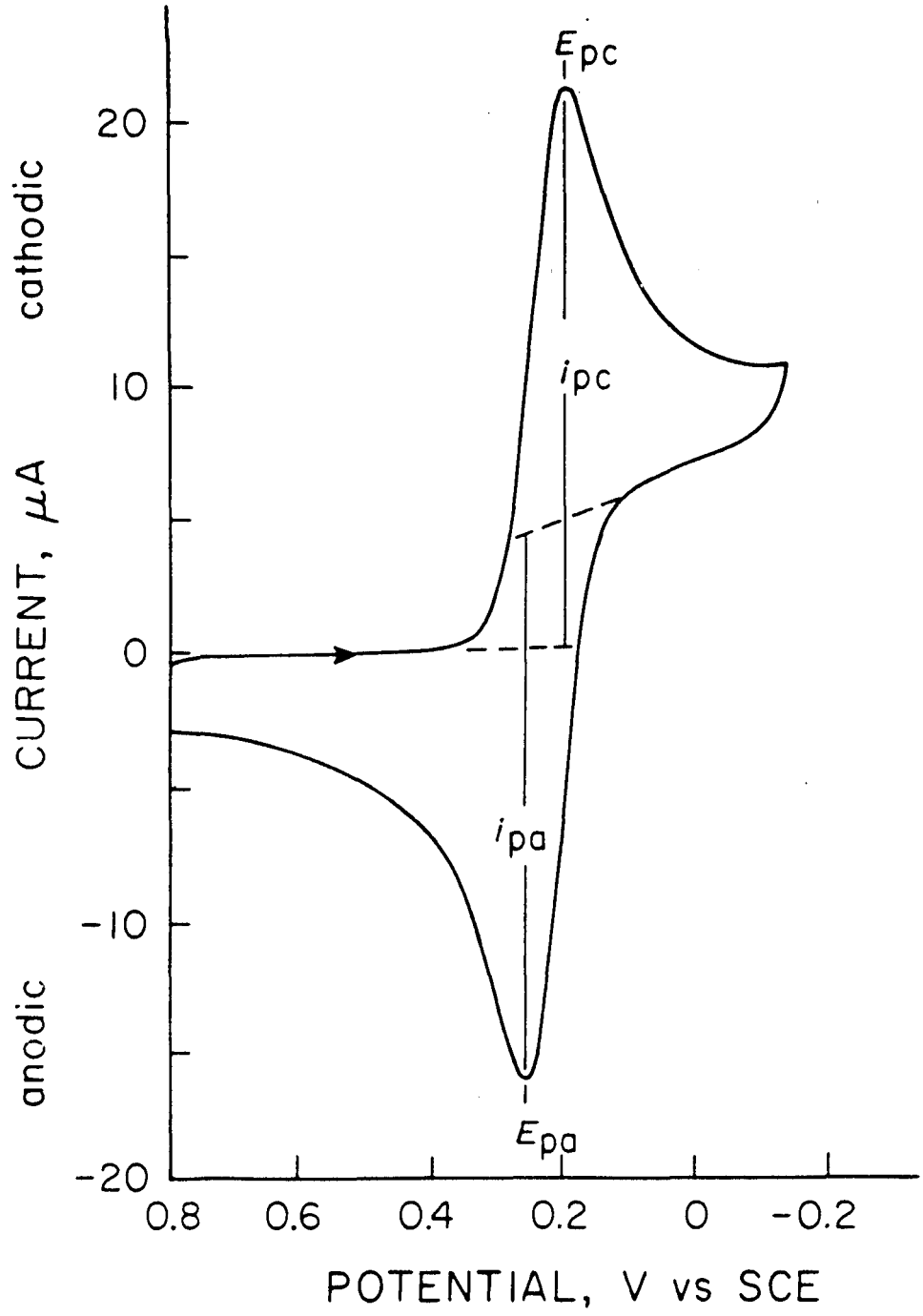

-0.2
0
0.2
0.4
0.6
0.8
Potential / V vs SCE
0
2
4
6
8
Time / s

Figure 9: Example of a typical cyclic voltammogram. Platinum electrode measuring 6mM $K_3Fe(CN)_6$ in 1 M KNO_3. Scan initiated at 0.8 V vs SCE in negative direction at 50 mV/s. (Reprinted, with permission, from Kissinger and Heineman.[55])


E_{pc}
20
cathodic
10
i_{pc}
CURRENT, μA
0
i_{pa}
-10
anodic
E_{pa}
-20
0.8
0.6
0.4
0.2
0
-0.2
POTENTIAL, V vs SCE

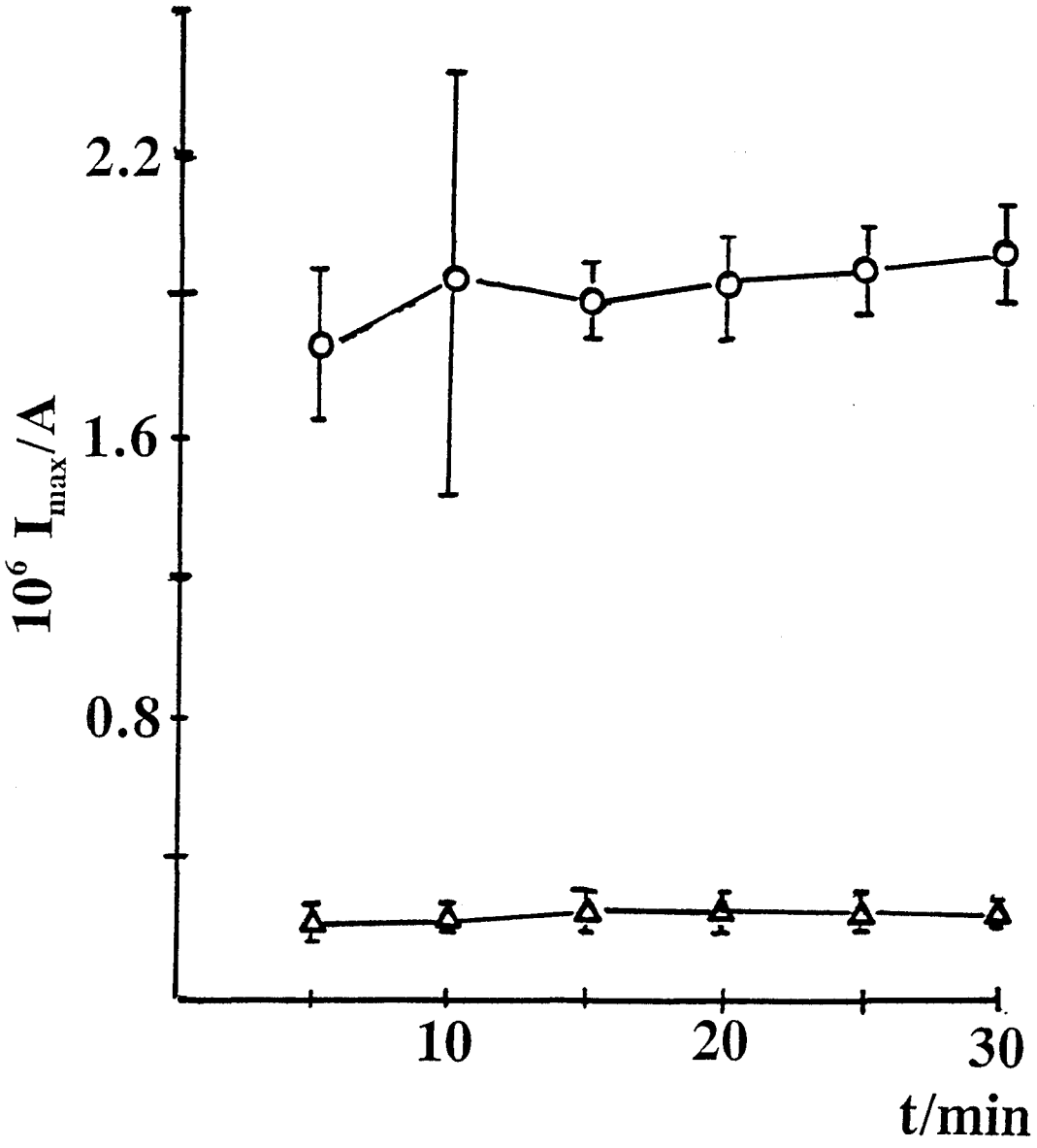
where n is the number of electrons transferred in the reaction, A is the electrode area, D_s is the diffusion coefficient of the species in solution, ν is the rate at which the potentials are scanned, and C^* is the concentration of the species in solution.

IV.2. Clay-Modified Electrode Studies

In clay-modified electrode studies, the current at a bare electrode and at a clay-modified electrode are measured and ratioed. Ratioing the two values compensates for differences in solution concentration and environmental factors. In order to relate this ratio to the diffusional properties of the clay film a number of conditions must be met.

First, the area of the two electrodes must match. The areas of the electrodes are determined through the Randles-Sevcik equation (see methods). Secondly, the probe ion must not interact with the clay film. The movement of the ion through the film must be through a purely diffusional path. Since the clay film is negatively charged, the anion $Fe(CN)_6^{3-}$ is used as the electroactive probe. Due to its small size and negative charge $Fe(CN)_6^{3-}$ does not interact with the clay film.[13] The clay film must also be stable. The stability of the clay film is confirmed by measuring the current at a CME over a period of time in different electrolyte concentrations. Since the current does not change, the clay film does not change and is thus, stable (Figure 10).[56] Finally, the measurement must be due to the clay film. To assure this is true, the diffusion layer which is generated by the electrochemical experiment must reside with the clay film. This is confirmed by generating plots of I_{pc} vs $\nu^{1/2}$ for different electrolyte concentrations. At

Figure 10: Effect of continuous cycling on current at a clay-modified electrode. (△) represents data collected in 0.7 M NaCl. (○) represents data collected in 0.2 M NaCl. (Reprinted, with permission, from Fitch and Du.[56])


2.2
1.6
0.8
10^6 I_{max}/A
10
20
30
t/min

some point in these graphs there will be a change in the slope of the line (Figure 11). This change in slope can be attributed to a change in the diffusion coefficient from a solution controlled diffusion coefficient to a diffusion coefficient controlled by the clay film (Equation 6). This change in control of the diffusion coefficient is due to a change in the thickness of the diffusion layer. As the time for an experiment increases, the thickness of the diffusion layer increases. At some point, it becomes so thick that it becomes thicker then the clay film. In order to assure that the diffusion layer resides within the clay film, a rapid scan rate is chosen. This ensures that the diffusion layer is thinner then the clay film and, is thus, controlled by the properties of the clay film.[56]

Electrochemical equations can be combined with those from soil science to show that the ratioed current is related to the diffusional properties of the clay film.[57] The area at a clay modified electrode is defined by the portion of the electrode available for the electrochemical reaction. This, in turn, is controlled by the size of the pores in the clay:

$$A_{cme} = \partial \Sigma b \qquad [7]$$

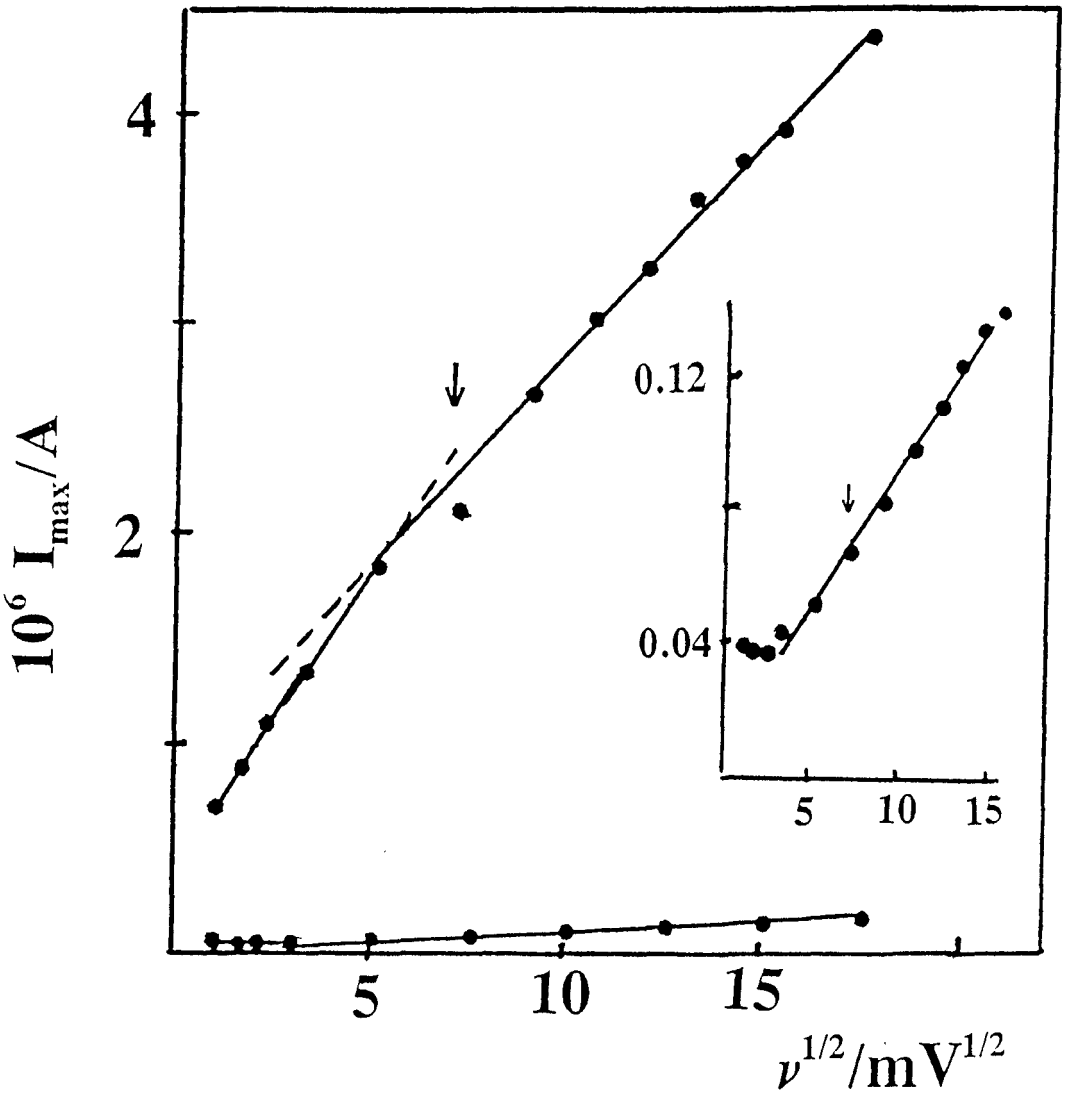
where ∂ is the cross-sectional area of the pores and b is the width of the pores.

The diffusion coefficient for a species in the clay film is different from that in solution. This difference is expressed as the tortuosity for diffusion in the clay film.

$$D_{cme} = \tau D_{solution} \qquad [8]$$

In which τ, the tortuosity, incorporates the non-perpendicular paths that the diffusing species must take, the change in viscosity of the solution in the clay film, and the drag that the clay walls exert on the diffusing species.

Figure 11: Scan rate dependence of the maximum cathodic current for 4mM $Fe(CN)_6^{3-}$ in 0.02 M NaCl (upper plot) and 2M NaCl at a CME. Arrows indicate inflection points for graphs. Inset: expanded graph for 2M NaCl. (Reprinted, with permission, from Fitch and Du.[56])


4
2
$10^6 I_{max}/A$
0.12
0.04
5
10
15
5
10
15
$\nu^{1/2}/mV^{1/2}$

The concentration of the diffusing species will also be different from that of the species in solution. This can be expressed as:

$$C_{cme} = \kappa C^* \quad [9]$$

where κ is the partition coefficient for the diffusing species.

If these equations are inserted into the Randles-Sevcik equation (Equation [6]), the equation for the current in a clay-modified electrode becomes:

$$I_{pcme} = (2.69 \times 10^{-5})n^{3/2}\partial\Sigma b(\tau D_{solution})^{1/2}\nu^{1/2}\kappa C^* \quad [10]$$

where all variables are as previously described. Ratioing this equation to that at the bare electrode results in:

$$\text{Ratio} = I_{pcme}/I_{pbare} = \partial\Sigma b\tau^{1/2}\kappa/A \quad [11]$$

This equation can be further simplified by recalling that κ is close to 1 for an excluded anion.[57]

$$\text{Ratio} = \partial\Sigma b\tau^{1/2}/A \quad [12]$$

Equation [12] tells us that the ratio is proportional to the interlayer distance. Alternatively, the ratio can be expressed as a function of the porosity of the clay film. The porosity of the film ,θ, is defined as the size of the clay pores divided by the area of the film or, in this instance, the electrode area:

$$\theta = \partial\Sigma b/A \quad [13]$$

As a result the ratio can be expressed as:

$$\text{Ratio} = \theta\tau^{1/2} \quad [14]$$

Therefore, the measured ratio current is a measure of the porosity of the clay film and the path that the diffusing species must follow.

Experimental evidence indicates that in SWy-1, a swelling 2:1 layer clay, the measured ratio is related to the interlayer spacing of the clay film. The first piece of evidence that this is the case is the correlation between CME studies on the dependence of ratio current on salt concentration and X-ray diffraction measurements of the dependence of interlayer spacing on salt concentration (Figure 12). Both the shape of the curve and the concentration where the measured spacing or ratio changes match. Additionally, the effect of different salts on the interlayer spacing in a CME is the same as the effects seen in X-ray diffraction studies (Figure 13). Finally, direct measurements of the interlayer spacings using a Synchrotron X-Ray diffractometer correlate interlayer spacing to ratio measurements (Figure 14). These results are, however, preliminary.

While for SWy-1 the ratio current is a measure of the interlayer spacing of the clay film, this is not always the case. In the early work that was done with clay-modified electrodes, polyvinyl acetate (PVA) was used in the preparation of the CME.[58] Later research indicated that this early work examined the defects present in the clay film rather then the interlayer region, or any other properties of the clay.[59] In this, and other work,[13,60] the importance of the clay film structure has been stressed. In order to assure that the experiment is studying the effect of the clay film, care must be taken to insure that the clay film is free of defects. In our laboratory this is done by preparing spin-coated clay-modified electrodes (SPCME)s. The act of spin drying the electrode ensures that the clay platelets are aligned in a regular manner.[59,60]

Figure 12: A) Plot of the ratio of the currents obtained at the CME and at the bare electrodes as a function of electrolyte concentration. B) X-ray diffraction data obtained for clay platelets as a function of NaCl (x) and Na_2SO_4 (o) concentration. (Reprinted, with permission, from Lee and Fitch.[13])

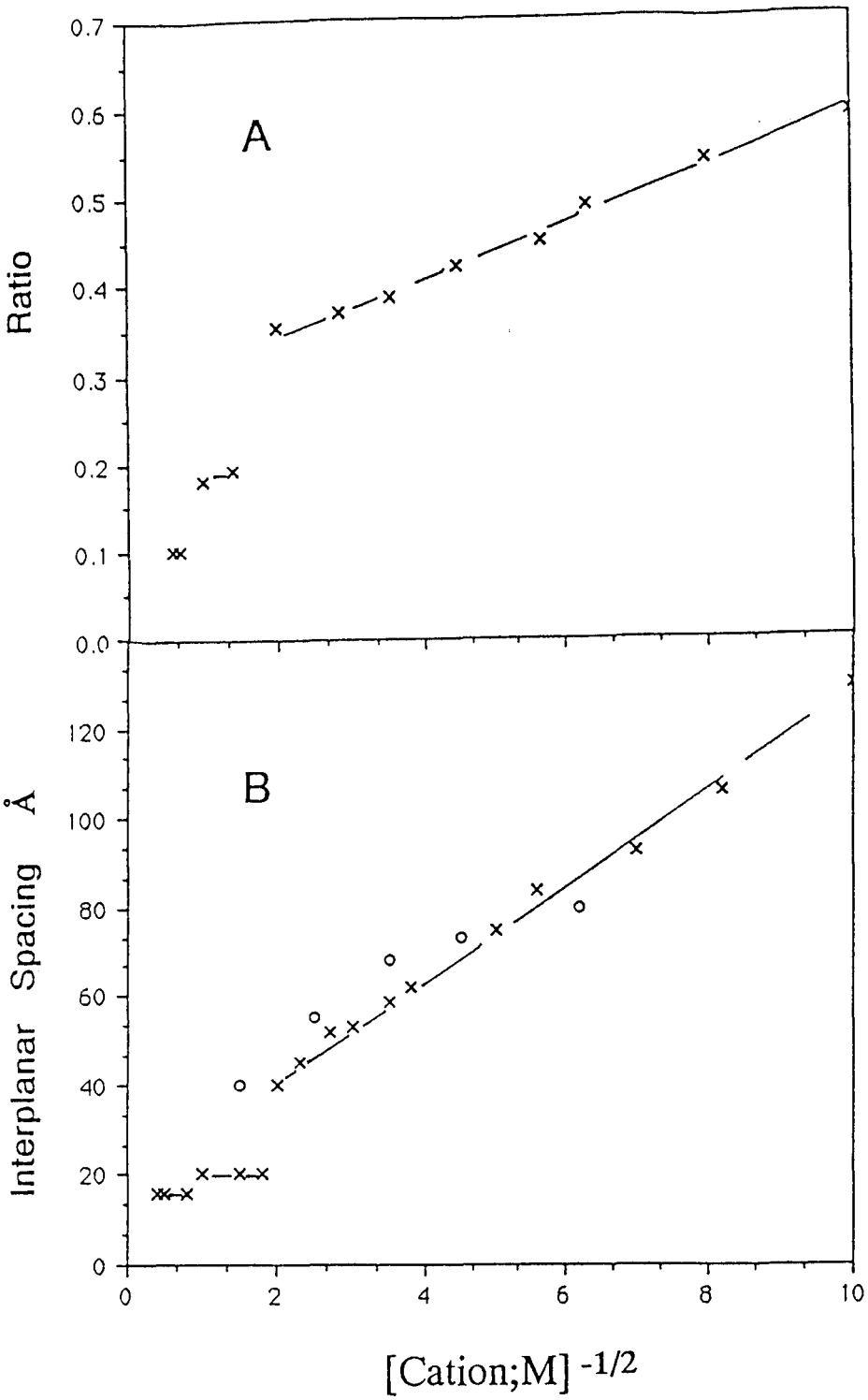

A
B
Ratio
Interplanar Spacing Å
[Cation;M] -1/2
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
120
100
80
60
40
20
0
0
2
4
6
8
10

Figure 13: Effect of salt type on the swelling of SWy-1. Figure (A) illustrtes the effect of cation type. In the figure (x) is LiCl, (o) is $CaCl_2$, (+) is KCl and (◇) is CsCl. Figure (B) represents the effect of anion. In the figure (x) represents NaCl and (◆) represents Na_2SO_4. Experimental conditions are 35 μg SWy-1, 4 mM $Fe(CN)_6^{3-}$. (Reprinted, with permission, from Lee and Fitch.[13])

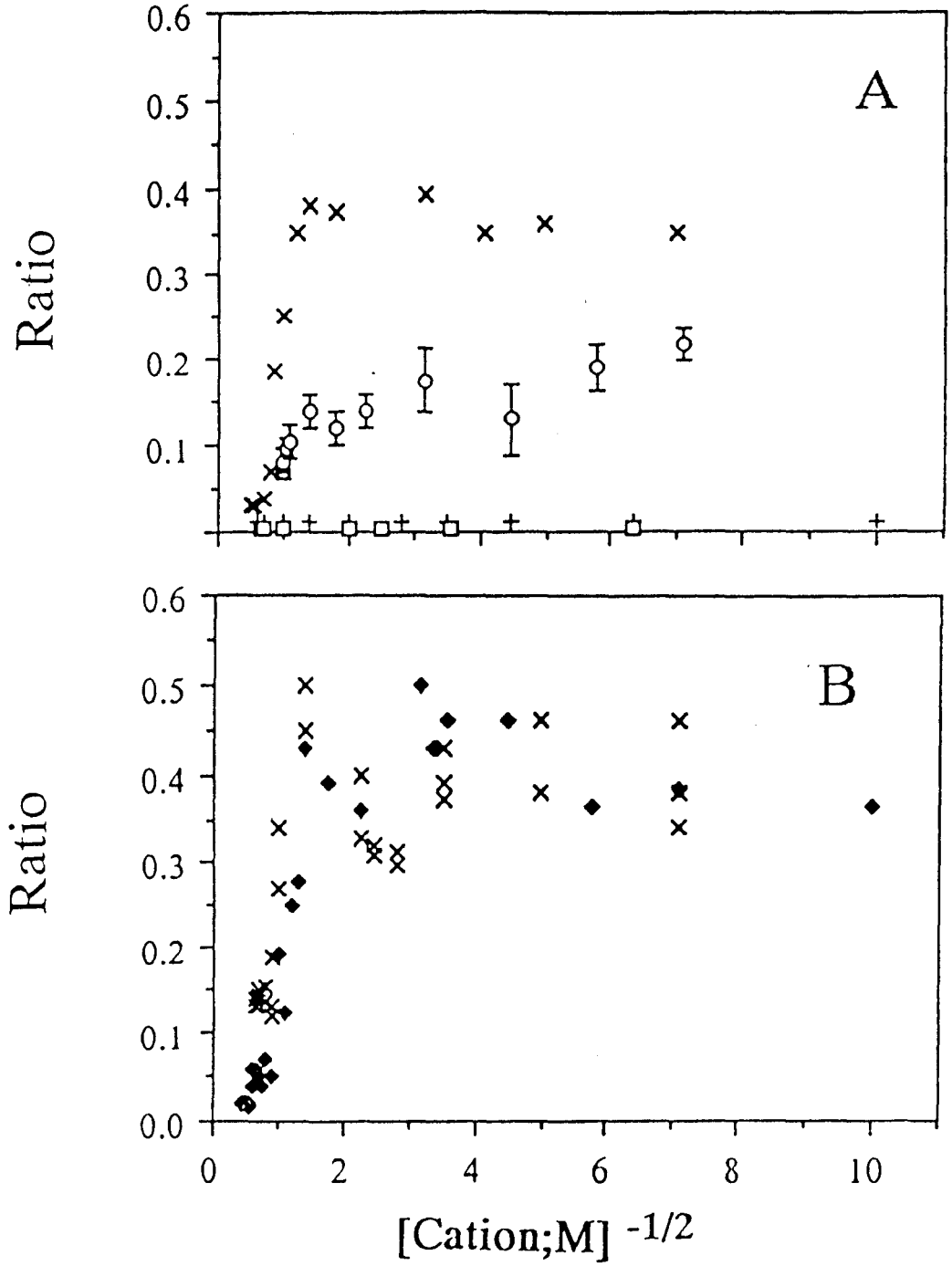
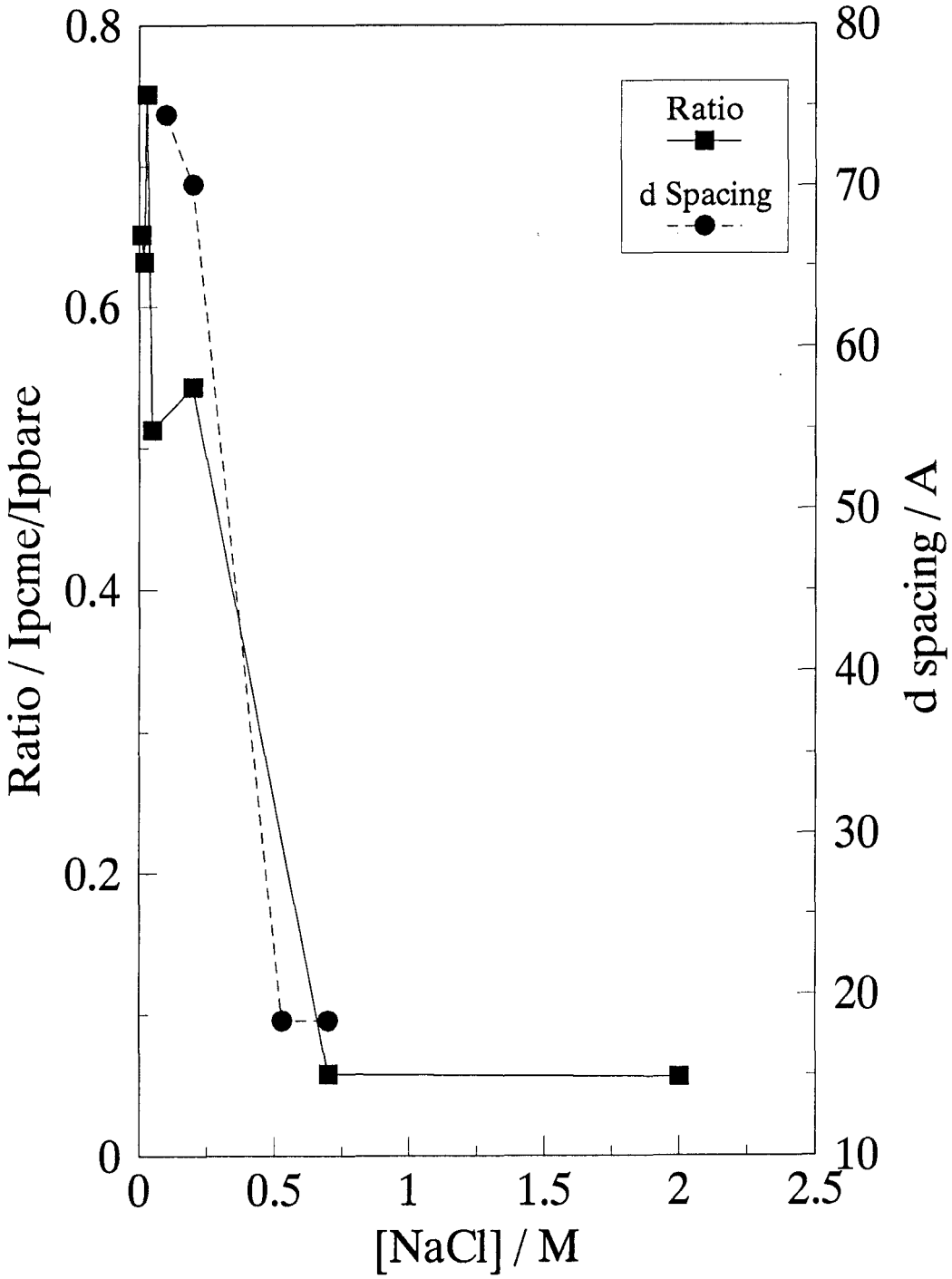

A
B
Ratio
Ratio
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
2
4
6
8
10
[Cation;M] -1/2

Figure 14: Comparison of preliminary synchrotron X-ray diffractometer data for interlayer spacing with ratio data. (□) represents ratio data obtained with a CME. (▵) represents measurements of interlayer spacing made with a synchrotron X-ray diffractometer.


0.8
0.6
0.4
0.2
0
0
0.5
1
1.5
2
2.5
80
70
60
50
40
30
20
10
Ratio / Ipcme/Ipbare
d spacing / A
[NaCl] / M
Ratio
d Spacing

In summary, the measured current at a clay-modified electrode is due to the effect of the modifying clay layer on the diffusional properties of the ion probe. If care is taken in the experimental design, these effects can be directly related to the porosity of the clay film.

V. Synopsis of Experiments

In this dissertation, the development of an automated system for use in CME studies is reported. The system allows the swelling response of a single clay film to be monitored. In previous experiments, a different clay film was used for each data point since, when a clay film is exposed to the air, irreversible changes may occur to the film structure. By using a single clay film, the response of the clay film can be examined without the errors inherent in clay film variability. Additionally, the use of a single clay film allows the response of the clay film to a series of different conditions to be followed. The system also incorporates the bare and the clay-modified electrodes into the same electrochemical cell. This arrangement can be compared to a dual beam spectrometer in that it incorporates the reference and the sample in the same system. Like a dual beam spectrometer, this allows for matching of experimental variables and reduces the time for an experiment in half. By combining a stepper motor and a computer, the response of the clay film is monitored from the moment it contacts the electrolyte solution and is continuously monitored until equilibrium is achieved. Multisweep cyclic voltammetry is used for continuous data acquisition. Due to the

computer there are virtually no limitations on time of data acquisition. A water bath and temperature probe are incorporated into later experiments for temperature control. Combined, these capabilities allow the porosity of the clay to be mechanistically probed.

The effect of clay type, electrolyte concentration, previous handling, and temperature on the diffusional properties of the clay film will be examined. Two types of experiments will be conducted. The first experiment examines the temporal nature of the clay's response to a low electrolyte concentration. In a low electrolyte concentration, a swelling clay film will expand its interlayer region from a collapsed regime to an expanded regime. By following this swelling with time, the nature of the process can be examined. These experiments will be used to examine the effect of temperature and prior handling on the response of the clay film. The second experiment examines the interlayer spacing within the clay film as a function of electrolyte concentration. Each clay type responds differently to different electrolyte concentrations. By combining the results from these two experiments, the nature of the interlayer expansion for each clay type is defined. The goal of these studies is to gain a better understanding of the factors that effect diffusion in a clay-modified electrode.

CHAPTER 2

EXPERIMENTAL METHODS

I.Experimental

I.1.Instruments

The electrochemical system was controlled by a Gateway 2000 386DX computer (N. Sioux City, SD). A Kiethley (Taunton, MA) MSTEP-5 dual stepper motor control board and DAS-HRES high resolution 16 bit analog-digital interface board were installed. The MSTEP-5 was connected to a Kiethley STA-Step Stepper Motor Driver and Screw Terminals Accessory Board via a CACC-200 interconnecting Cable. This in turn was connected to a model 23D-6102A 5.0V DC 1 Amp STEP-MOT1 Stepper Motor from Kiethley. Power was supplied to the STA-Step by a TrippLite (3 Amp, 12V DC) power supply. The stepper motor was attached to an X-Y positioner (Deadal, Harrison City, PA). The DAS-HRES was connected to the STA-HRES screw terminal by a CDAS-2000 cable. A Nicolet 4094A Digital Oscilloscope (Madison, WI) was used to visually monitor the electrochemical reaction. For the temperature studies, the system was modified by the addition of a circulating water bath (Fisher Scientific, Pittsburgh, PA) and a thermocouple. The temperature of the solutions was monitored inside the cell with a T-type thermocouple (Cole-Parmer, Skokie, IL) attached to a linearized thermocouple input module inserted into a STA-1360 screw module (Kiethley) which was connected

to the computer through the DAS-HRES. The program for data acquisition was written in Microsoft GW-Basic version 3.23 incorporating machine language programs which came with the software from Kiethley. The programs for data manipulation and output were written in Microsoft QuickBasic version 4.5.

Sample weighings were performed on a Sartorius Model 2443 analytical balance. Deionized water was obtained from an E-pure still run at 17.7 ohm·cm (Barnstead, Dubuque, IA). Clay samples were stirred on a VWR Model 320 magnetic stir plate (West Chester, PA) and centrifuged in a Sorvall RC-5B Refrigerated Superspeed Centrifuge equipped with a GSA rotorhead (Dupont Instruments). A Flexi-Dry lyophilizer from FTS Systems, Inc (Stone Ridge, NY) was used to freeze-dry the clay samples. A Malvern 3600 particle size analyzer (Malvern Instruments, Southborough, MA) equipped with a lens with a focal length of 63mm and a beam length of 14.3mm was used for particle size analysis. A Model 16 laboratory oven (Precision Scientific Inc., Chicago, IL) and a Thermolyne Type 1400 Furnace (Dubuque, IA) were used when needed.

An EG&G PAR 175 universal programmer coupled with a EG&G PAR 179 potentiostat (Princeton Applied Research, Princeton, NJ) were used for the electrochemical measurements. Potentials were measured against a Saturated Calomel Electrode (SCE). In the electrode characterization experiments, a EG&G Model RE0091 X-Y recorder was used in conjunction with the programmer and the potentiostat.

Electrodes were constructed in-house from 0.040 inch diameter Pt wire (D.F. Goldsmith, Evanston, IL) sealed in 0.750 inch diameter soft glass. Electrical connections

were made with a copper pin joint soldered to copper wire. Electrodes were polished on a Buehler ECOMET III Grinder/Polisher from Buehler (Lake Bluff, IL). Electrodes were sonicated in a Branson 1200 ultrasonic cleaner from Branson Utrasonics Corporation (Danbury, CT). Spin coated clay samples were prepared on an MSR Analytical Rotor with a MSR Speed Controller from Pine Instrument Company (Grove City, PA). Clay solutions were applied via a Hamiliton 10 μL microsyringe (Fisher Scientific). Clay-modified electrodes were examined with an American Optical Corporation (Buffalo, New York) Stereoscope. Scanning Electron Microscopy was performed on a Stereoscan 240 Scanning Electron Microcope from Cambridge Instruments Incorportated (Lica, Deerfield, IL). A Hummer VI Sputtering system (Anateck Limited, Alexandria, VA) was used to coat the films with palladium.

I.2. Chemicals and Clay Samples

Sodium chloride, sodium cyanide, triethanolamine, ethylenediaminetetraacetic acid (EDTA), ammonium chloride, ammonium hydroxide, calcium chloride, calmagite, and potassium chloride were purchased from Fisher (Pittsburgh, PA). Potassium ferricyanide was purchased from Aldrich (Milwaukee, WI). Sodium ferricyanide was from City Chemical Corporation (New York, NY). All chemicals were used as received. SWy-1, STx-1, SAz-1, SHCa-1, and KGa-1 were obtained from the Source Clays Repository at the University of Missouri in Columbia, MO. The clays were purified prior to use. Laponite was obtained from Southern Clay Products, Inc, Gonzales TX. This clay is a synthetic trioctahedral smectite and was used as received.

Dialysis tubing from Spectra/Por (Fisher Scientific) with a MWCO of 6-8,000 was treated before use. The tubing was prepared for use by boiling in a weak EDTA solution for 2 hours, a weak sodium carbonate solution for 1 hour, and finally, deionized water for 1 hour.

II. Procedures

II.1. Clay Sample Purification

Clays were purified according to the manner of Jackson.[61] Approximately 15 grams of clay were suspended in 450 mL of deionized water and stirred for 48 hours. The suspension was centrifuged for 35 minutes at 3500 rpm and 20°C. The supernatent was collected. Sodium exchanged clays were prepared according to the method of Kamat et al.[62] The supernatent was diluted to twice its volume in 2 M NaCl. This solution was stirred for 36 hours then centrifuged for 45 minutes at 7000 rpm and 20°C. The clays were resuspended in 2M NaCl and the above procedure was repeated twice. After the third rinse the clays were resuspended in deionized water. The clay solutions were dialyzed to remove any excess ions. Dialysis was performed until no precipitate was found with 0.2M $AgNO_3$. The resultant clay solutions were lyophilized to remove excess water.

II.2. Preparation of the Solutions

Solutions were prepared by weighing all species on an analytical balance. Solutions are brought to volume in volumetric flasks with deionized water.

Clay solutions were prepared on a weight to volume basis. Solutions were prepared fresh weekly.

II.3.Preparation of the Calcined Clay Samples

The Thermolyne furnace was heated to 1500°F. The dial was then set at 3 to maintain this temperature. A porcelain crucible was placed in the oven for 20 minutes to burn off any residual dirt. After the crucible cooled, approximently 2 grams of sodium exchanged freeze dried SWy-1 were placed in the crucible. The crucible was placed in the oven for 30 minutes. After cooling, the clay was transfered to a 1 ounce small jar. Glass beads were added to the jar and the jar was rotated to break up the clay particles. After the desired particle size was obtained, the balls were removed from the jar with tweezers. The sample was stored in a dessicator until used.

II.4.Electrode Cleaning

All working electrodes were polished prior to the beginning of an experiment. Polishing was performed with the polisher set to a polishing speed of 0.8 DC milliamperes. A felt polishing pad was used with a 0.2 μ alumina slurry and copious amounts of deionized water. This proceedure was performed for 1 minute. The electrodes were then rinsed to remove excess alumina in the sonicator for 30 seconds. Electrodes were dried with a Kimwipe paper tissue.

II.5.Preparation of the Spin-Coated Clay-Modified Electrode (SPCME)

The freshly cleaned electrode was inverted and placed in a rubber cork hollowed to accommodate the electrode. The other end of the cork was hollowed to attach to the top of the MSR spinner. The postion of the electrode was adusted to ensure an even rotation. The clay suspension was sonicated for 5 minutes then a 1 μL sample was applied over the platinum portion of the electrode. The electrode was rotated for 20 minutes at 800 rpm. The resultant clay film was examined for cracks under the microsope.

II.6.Electrochemical Experimental Setups

II.6.1.Standard Electrochemical Setup

The EG&G programmer was coupled with the potentiostat. The voltage from the programmer was run into the potentiostat and into the X axis of the X-Y recorder. The potentiostat controlled the potential in the cell and monitored the current at the working electrode. The current was then output to the Y axis of the X-Y recorder.

II.6.2.Computerized Electrochemical Setup

The electrochemical cell was a round glass cell with a curved stem at the bottom of the cell for solution input. The top of the glass cell was a 0.5 inch thick piece of plexiglass drilled to accommodate the electrodes. A piece of 0.5 inch thick plexiglass was placed on the bottom of the glass cell and the top and bottom were connected to ensure that the top was securely attached to the cell. The counter electrode was a piece

of platinum inserted through a septum and the reference electrode was a standard sized SCE. Solution was input into the cell using N_2 pressure. Solution was removed from the cell with a 50 mL syringe. A diagram of this cell is shown in Figure 15A.

The electrodes were inserted into the cell top. The remaining electrodes were inserted into the cell. The working electrodes were connected to the stepper motor through an "L" shaped piece of plexiglass. One end of the plexiglass was screwed into the x-y positioner. The electrodes were inserted through universal teflon adapters (Kontes, Vineland, MD) and securely attached to the other end. All electrochemical connections were made. The programmer voltage output was run into the potentiostat and into the DAC. The bare electrode current was run through a current-to-voltage converter (constructed in house) and into the DAC. The CME current was run through the potentiostat and into the DAC. A diagram of this system is shown in Figure 16A. The computer program was adjusted to the desired sampling rate, and other parameters. The solution was input into the cell. The electrodes were lowered into the solution, the programmer was triggered and data collection begun. All experiments were run at 0.8V to -0.2V vs SCE at a scan rate of 500 mV/s.

II.6.3.Computerized Electrochemical Setup with Temperature Control

For the temperature controlled studies a water jacketed cell was used. The top of the glass cell consisted of two 0.5 inch thick spacers of plexiglass. Attached to the top and the bottom of the spacers were 1/8 inch thick plexiglass pieces. The top piece secured the entire piece to the top of the cell. The bottom piece was drilled to

Figure 15: Electrochemical cells used in computerized and temperature controlled experiments. A) Cell used for computerized experiments. B) Cell used for temperature controlled experiments. In the figures (P) is the x-y positioner that is controlled by the stepper motor. (L) is the plexiglass attachment that connects the x-y positioner to the working electrodes. (S) is the working electrodes. (C) is the counter electrode. (R) is the reference electrode. (T) is the cell top. In Figure (A), the solution outlet is through the top and it is not shown for the sake of clarity. In Figure (B), the solution inlet is a side arm inlet similiar to that shown in (A). It is also not shown for the sake of clarity.

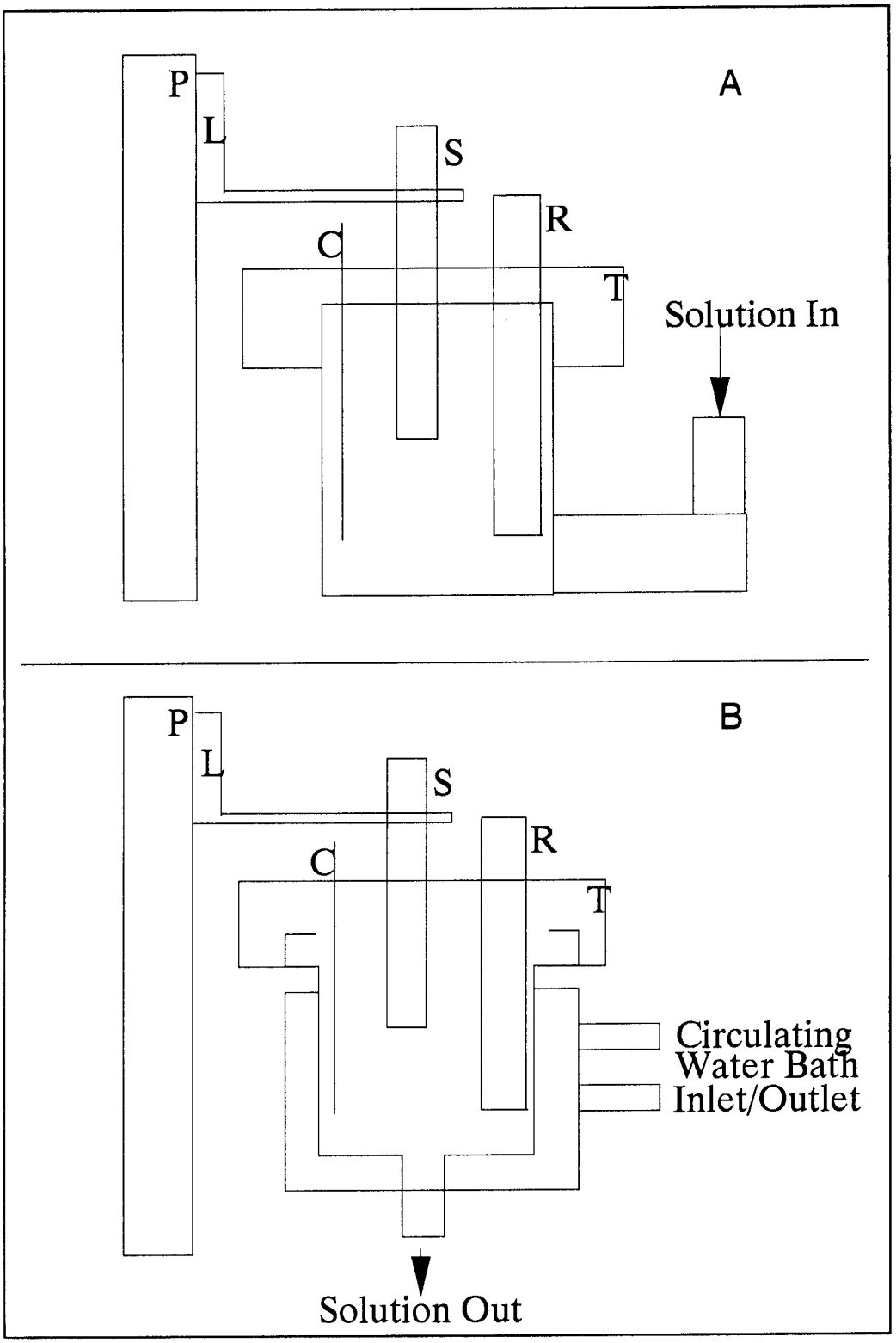
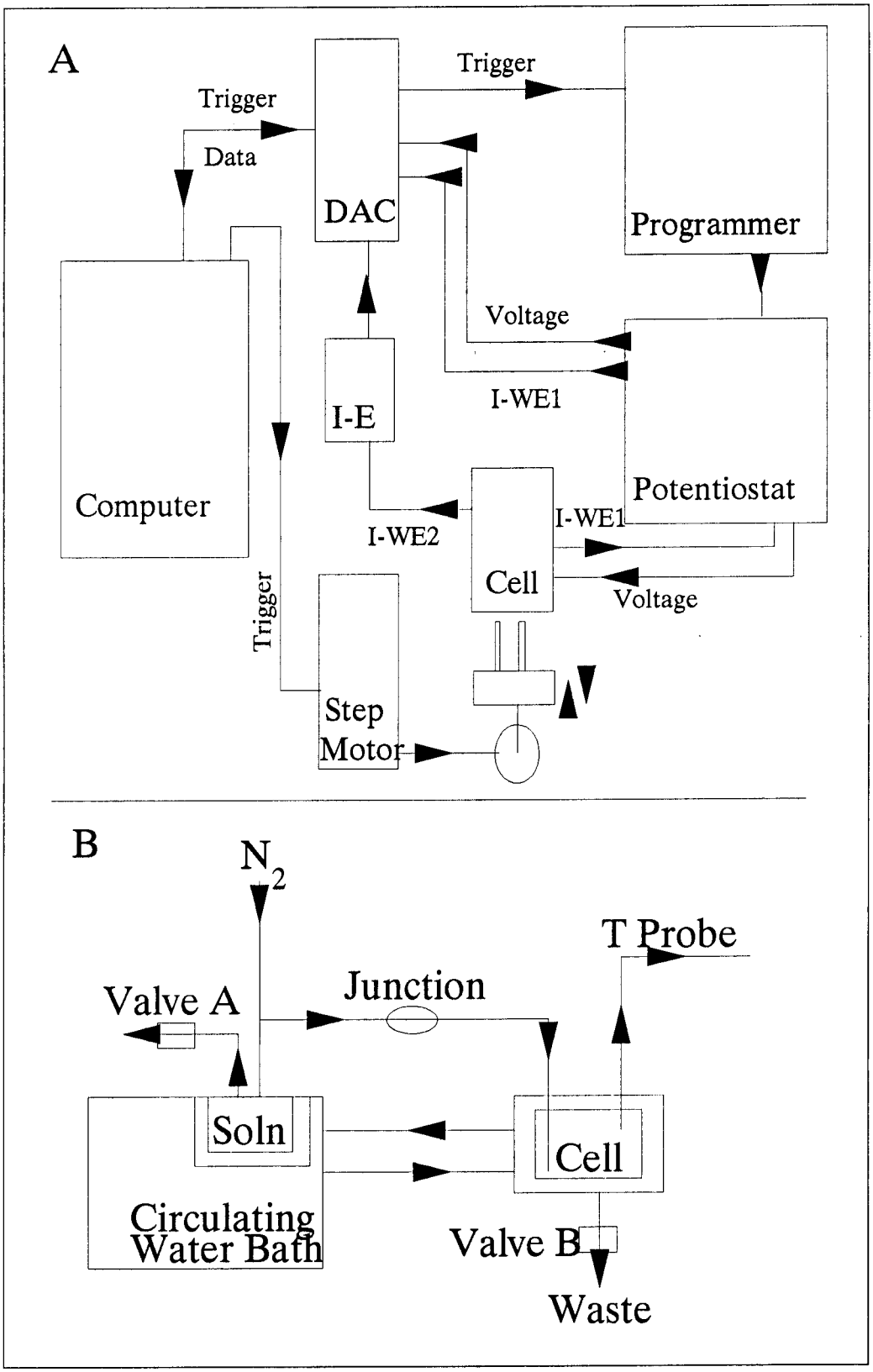

A
P
L
S
R
C
T
Solution In
B
P
L
S
R
C
T
Circulating
Water Bath
Inlet/Outlet
Solution Out

Figure 16: Diagram of computerized system. A) General diagram. B) Diagram showing temperature control modifications.


A
Trigger
Data
DAC
Trigger
Programmer
Voltage
I-WE1
I-E
Computer
Potentiostat
I-WE2
I-WE1
Cell
Voltage
Trigger
Step
Motor
B
N2
T Probe
Valve A
Junction
Soln
Cell
Circulating
Water Bath
Valve B
Waste

accomodate the following: two working electrodes; the piece of platinum and the septum which served for the counter electrode; a standard sized SCE; a septum and a glass rod through which nitrogen was purged; and a glass rod through which the temperature probe was inserted. Solution was input into the cell through a tube which led to the bottom of the cell. Solution was removed from the cell through a drain in the bottom of the cell. A diagram of this cell is shown in Figure 15B. The temperature of the incoming solutions was controlled by placing the solutions inside the water bath and by monitoring the temperature on the water bath. The electrode movement and monitoring of data were as described in II.6.2. Modifications to the computerized system are shown in Figure 16B.

III. Characterization of Working Electrodes

In order to use the dual-electrode set-up, the areas of the two working electrodes must match. In order to determine the areas of the working electrodes, the Randle-Sevich equation was used (See Chapter 1, Equation 1). Six different scan rates were used. A 1M NaCl solution with 2 mM $Fe(CN)_6^{3-}$ as analyte was used. The electrodes were cleaned as described in II.4. The electrochemical setup was described in II.6.1. Three replicates were performed at each scan rate. Electrodes were freshly polished prior to the measurement. The initial scan was used for all calculations.

IV. Characterization of Clays

IV.1. Determination of Particle Size

Particle sizes were determined via light scattering. The clay sample was dispersed in water in the sample cell with stirring. The concentration within the cell was adjusted to optimal with water.

IV.2.Determination of Moisture Content

The temperature of the oven was adjusted to 105°C. Cleaned weighing bottles and caps were placed in the oven for 1 hour. They were removed from the oven and weighed hot. Clay was quickly weighed into the bottle and the bottle was returned, uncovered to the oven. After 2 hours the bottles were covered with the hot caps. They were removed from the oven and a hot weight was taken. The bottles were returned to the oven, allowed to reheat, and another weight was taken. The final weight was an average of three weighings. To determine the moisture content of the clay the weight loss was divided by the initial clay weight and multiplied by 100.

IV.3. Determination of Calcium Content in SAz-1

Calcium analysis was performed on the sodium exchanged and on an un-exchanged SAz-1 sample. The method of Diehl[63] was used. The EDTA was first standardized against a standard $CaCl_2$ solution. A 50 mL aliquot of solution was pippetted into a 250 mL erlymeyer flask. Approximately 0.1 g of ascorbic acid, 10 mL of pH 10 buffer, 5 mL of a 5% NaCN solution, 5 mL of a 20% triethanolamine solution and 4 drops of calmagite indicator were added. The solution was titrated with the EDTA. This procedure was repeated three times. Triplicate samples of the clays were

then titrated with the EDTA solution. In this instance, a 10 mL buret was used to increase the accuracy of the titration. A 0.5 mL sample of a 35 g/L suspension of the sodium-exchanged sample and a 0.2 mL sample of a 35 g/L suspension of the untreated sample was used. The reagent amounts were scaled according to the sample size.

V. Optimization of Computerized Electrochemical System

V.1. Determination of Time Needed to Obtain Equilibrium Conditions in Clay Film

The clay solution was prepared to a concentration of 35 g/L. The SPCME was prepared in the manner described in II.5. The electrochemical setup was described in II.6.2. A 1 M NaCl with 2 mM $Fe(CN)_6^{3-}$ solution was input into the cell. The electrodes were allowed to equilibrate for a given period of time. The solution in the cell was then switched to 0.7 M NaCl with 2 mM $Fe(CN)_6^{3-}$ and the above proceedure was repeated. Subsequently, 0.5 M, 0.3 M, and 0.1 M NaCl solutions with 2 mM $Fe(CN)_6^{3-}$ were input into the cell. The first ten then every fifth scan of data were collected. Experiments were performed with 5 minute, 8 minute, 15 minute, 30 minute and 45 minute equilibration times. Each experiment was repeated a minimum of three times.

V.2. Determination of Sampling Rate to Use for DAC

The electrochemical setup was assembled in the standard manner. Scan rates and sampling frequencies were input into the computer. The computer then calculated the

number of points to collect and determined the maximum sampling rate it could use. A scan was collected at the input parameters and visually evaluated.

VI. Studies on SWy-1

VI.1. Effect of Clay Film Thickness on Response of SWy-1 Clay Film

Clay solutions were prepared on a weight to volume basis to concentrations of 17.5, 26.2, and 35 g/L. The SPCME was prepared as described in II.5. For the 75 μg sample, 2 drops of the 35 g/L solution were layered onto the electrode surface. As a control for this sample, a 35 μg film was formed in a similiar manner from 2 1 μL drops of the 17.5 g/L solution. After the clay films were formed, the SPCME and the bare electrode were inserted into the electrochemical setup described in II.6. A 4 M NaCl solution with 2 mM $Fe(CN)_6^{3-}$ was added. The electrodes were allowed to equilibrate in this solution for 45 minutes. The solution was then changed to 0.1 M NaCl with 2 mM $Fe(CN)_6^{3-}$ and the response of the electrodes was followed for 45 minutes. Every scan was collected for both the 4 M solution and the 0.1 M NaCl solution. At least three replicates were performed.

VI.2. Response of a Dry SWy-1 Clay Film to 0.1M NaCl

The clay solution was prepared to a concentration of 35 g/L. The SPCME was prepared as described in II.5. The electrochemical setup was as described in II.6.2. A 0.1 M NaCl solution with 2 mM $Fe(CN)_6^{3-}$ was input into the cell. The response of the

electrodes was followed for 45 minutes. The first twenty, then every other, scans were collected. The experiment was repeated at least three times.

VI.3. Effect of Temperature on SWy-1 Clay Film Response

The conditions used in this experiment were the same as VI.2., with the exception of the electrochemical setup. The electrochemical setup for this experiment is described in II.6.3. The temperature of the solution was determined by equilibrating the solution for 20 minutes in a glass sample cell in the water bath. The water-jacketed cell was also equilibrated to the desired temperature by circulating water from the water bath through the cell for at least 20 minutes prior to the beginning of the experiment. In this experiment, every other scan was collected. The temperature of the solution inside the cell was monitored and the temperature of the water bath was adjusted as necessary. At least 10 replicates of this experiment were performed for each temperature.

VI.4. Response of a Swollen SWy-1 Clay Film to a Concentrated Electrolyte Solution

The experimental conditions were the the same as those described in VI.2. After the 45 minute equilibration period in 0.1 M NaCl, the solution was changed to a solution containing a 4 M concentration of either NaCl or KCL with 2 mM $Fe(CN)_6^{3-}$ and the response was followed for an extended period of time. The first ten, then every tenth, scans were collected. The experiment was repeated at least three times.

VI.5. Response of a SWy-1 Clay Film to Changing Electrolyte Concentrations

The conditions used in this experiment were the same as those described in V.1. except a 45 minute equilibration period was used for all experiments.

In the hysteresis experiments, the same procedure was followed. After the 0.1 M solution, however, the solution concentrations were gradually increased in the cell. Solutions with 0.3 M, 0.5 M, 0.7 M, 1 M, 2 M, 3 M, and 4 M NaCl along with 2 mM $Fe(CN)_6^{3-}$ were sequentially input into the cell and equilibrated for 45 minutes. All experiments were repeated at least three times.

VII. Studies on Two Component Clay Films

VII.1. Response of Dry Clay Films to 0.1M NaCl

The conditions used in this set of experiments were identical to those of VI.2. The only difference was that 2 clays were used in the 35 g/L clay solution. The weight of each clay in the mixture varied according to the percentage of the clay desired in the final mixture.

VII.2. Response of Clay Films to a Change in Electrolyte Concentration

The conditions used in this set of experiments were identical to those of VI.5. The only difference was that 2 clays were used in the 35 g/L clay solution. The weight of each clay in the mixture varied according to the percentage of the clay desired in the final mixture.

VII.3. Scanning Electron Microscopy (SEM)

A 0.5 inch diameter aluminum stub was polished on the polishing wheel and sonicated. The stub was then inserted into a rubber cork hollowed out to fit the end of the stub. The other end of the cork was attached to the MSR pine rotatator. The clay mixture was sonicated 5 minutes to evenly disperse the different clays. A 50 μL drop of the clay mixture was applied to the aluminum stub with a 50 μL Hamilton syringe. The stub was rotated for 15 minutes at 250 rpm, 10 minutes at 600 rpm, and 30 minutes at 800 rpm. The resultant clay film was stored in a dessicator for at least 1 week prior to use to ensure that the film was well dried. The clay films were inserted into the sputter coater to coat with a 3 μm thick palladium layer. The samples were then placed into the SEM vacuum chamber. An energy beam of 3 kV with a magnification of 81.7x was used for all samples.

VIII. Studies on Three Component Clay Films

VIII.1. Response of Dry Clay Films to 0.1M NaCl

The conditions used in this set of experiments were identical to those of VI.2. The only difference was that 3 clays were used in the 35 g/L clay solution. The weight of each clay in the mixture varied according to the percentage of the clay desired in the final mixture.

VIII.2. Response of Clay Films to a Change in Electrolyte Concentration

The conditions used in this set of experiments were identical to those of VI.5. The only difference was that 3 clays were used in the 35 g/L clay solution. The weight of each clay in the mixture varied according to the percentage of the clay desired in the final mixture.

IX. Studies on Laponite

IX.1. Response of a Laponite Clay Film to Changing Electrolyte Concentrations

The conditions used in this set of experiments were identical to those of VI.5.

IX.2. Response of a Laponite Clay Film to Switching between 1 M NaCl and 0.1 M NaCl Electrolyte Concentrations

The clay solution was prepared to a concentration of 35 g/L. The SPCME was prepared as described in II.5. The electrochemical setup was as described in II.6.2. A 1 M NaCl solution with 2 mM $Fe(CN)_6^{3-}$ was input into the cell. The response of the electrodes was followed for 45 minutes. The solution was then changed to 0.1 M NaCl and the electrodes' response was followed for 10 minutes. The solution was then switched back to 1 M NaCl. This proceedure was repeated for a total of ten measurements in each solution. The first twenty, then every fifth, scans were collected.

CHAPTER 3

RESULTS AND DISCUSSIONS

I. Instrumentation

Before using the dual electrode system, the areas of the two electrodes must be matched. The areas of the electrodes were determined with the Randles-Sevich equation. The area of the electrode used as a CME is $7.47 \pm 1.06 \times 10^{-3}$ cm^2. The bare electrode area is $7.47 \pm 1.11 \times 10^{-3}$ cm^2. Additionally, the conditions at the two electrodes must be identical. The working electrode in a conventional three electrode system is maintained as ground. Maintaining the second working electrode as ground ensures that conditions at the two electrodes are identical. The current for the second working electrode is run through an I-E converter. The current for the first working electrode is run through the commercial amplifier. The amplification for the I-E convertor and for the commercial amplifier were calibrated and found to be 9.96×10^{-6} A/V and 10×10^{-6} A/V respectively.

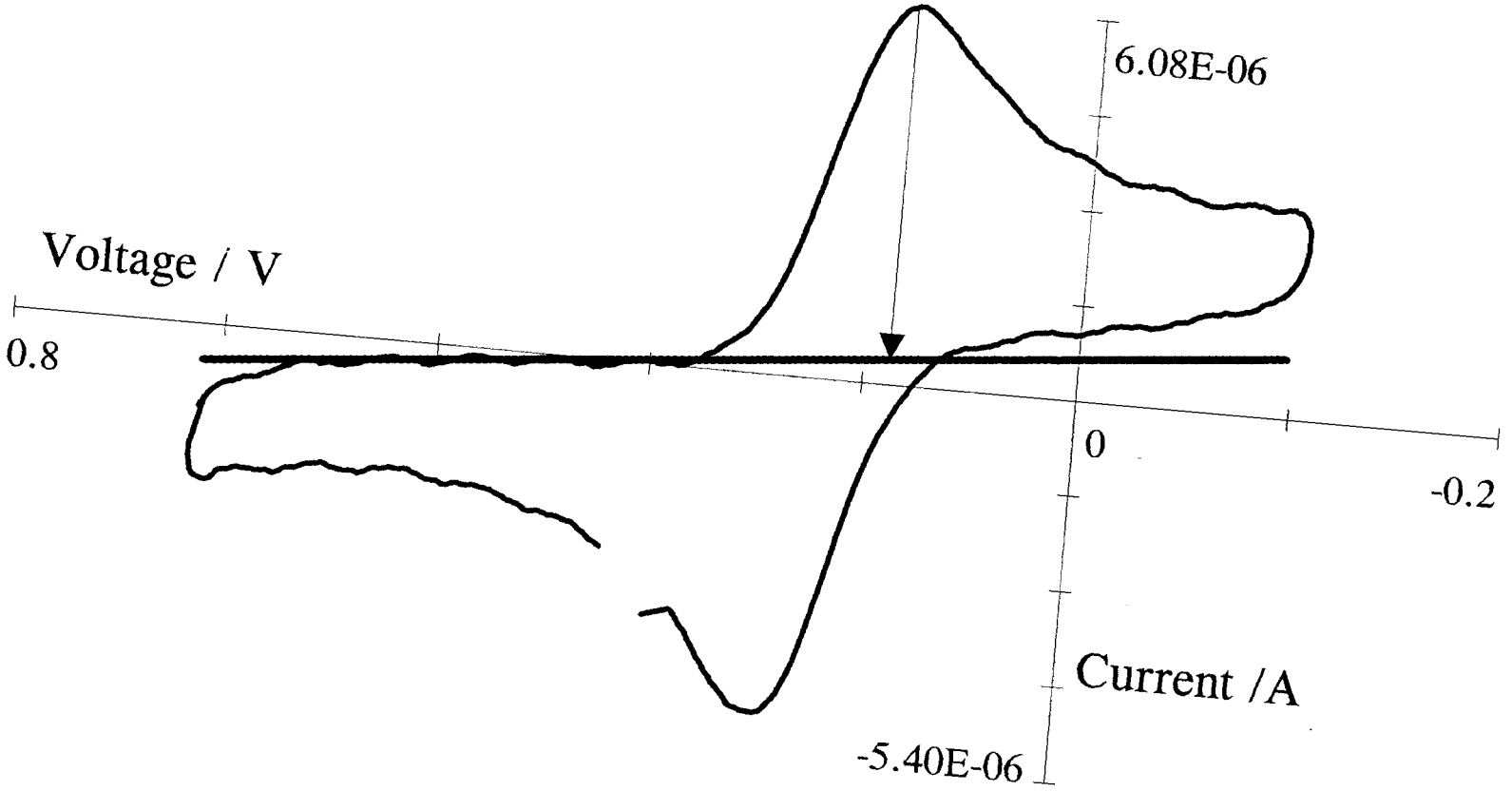
Multi-sweep cyclic voltammetry at a relatively fast scan rate is performed in order to accurately follow the response of the clay film. A one volt potential window coupled with a scan rate of 500 mV/s, allows the response of the clay film to be sampled every 4 seconds. A 500 Hz sampling frequency means that a data point is collected every 0.002 seconds. Since there are three channels to sample, each channel is sampled

every 0.006 seconds. At this sampling rate, the shape of the cyclic voltammogram is well defined (Figure 17).

The program for data acquisition is written in GW-Basic. While this is an older program, it readily interfaces with the machine language programs that came with the hardware. A serious limitation in GW-Basic, however, is the size of the active workspace. This space is limited to 64K bits. During data acquisition, the data are initially stored to RAM space. They are then called into the workspace and exported for later use. Because the data must be called into the workspace before exportation, the size of a data file is limited to the size of the workspace, or 64K bits. If a scan is 4 seconds long, then, with a sampling rate of 500 Hz, 6000 points or 12000 bits are collected per scan. This is much less than the size of the workspace and no problems with file size are encountered. At a slower scan rate, however, the limitation in workspace size becomes a problem. For example, at a 50 mV/s scan rate, with a 1 V potential, window, and a 500 Hz sampling rate, 60000 or 120000 bits of data are collected per scan. To collect less then 64K bits of data, a slower sampling rate must be used. However, at too slow a sampling rate, the number of points collected is not enough to provide an accurate signal to noise ratio. As a result, an experimentally determined lower sampling frequency of 160 Hz exists. This sampling rate corresponds to a scan rate limit of 50 mV/s. Below this scan rate, the cyclic voltammogram is too noisy to accurately determine the peak currents.

At the rapid scan rates used in the following experiments, no problems with data acquisition were encountered. The data is acquired and exported to a file where it is

Figure 17: Typical cyclic voltammogram. CV has been boxcar averaged to smooth the curve. The extrapolated baseline and peak cathodic current are shown. Experimental conditions are bare electrode, 1 M NaCl, 2 mM $Fe(CN)_6^{3-}$, 500 mV/s scan rate, 0.8 to -0.2 V potential window.


6.08E-06
Voltage / V
0.8
0
-0.2
Current /A
-5.40E-06

manipulated after the completion of the experiment. Data manipulation consists of baseline extrapolation, curve smoothing, determination of the peak currents for the anodic and cathodic peaks, and determination of the ratio of the peak cathodic currents for the bare and the clay-modified electrodes.

The first step in data manipulation is determination of the baseline current in the cyclic voltammograms. A baseline current can be extrapolated for each of the scans or for a representative scan. In practice, a representative scan is chosen well into the file at a point where equilibrium has been somewhat established. The baseline current is determined through visual evaluation of a line calculated for a specified area of the voltammogram. Linear regression is performed on the points in this area to determine the line and the slope and the y-intercept of the line. These data are then stored and used to determine the baseline current for each scan in the file.

During data manipulation, each individual scan is called up and the data is first smoothed via a boxcar Gaussian smoothing routine. The peak current values and the voltages at which these currents occur are determined. The voltages at which the peak currents occur are plugged into the formula for the best fit baseline to determine the baseline current. This value is subtracted from the peak current value. The peak cathodic currents for the CME and for the bare electrode are then ratioed to normalize the data. Figure 17 shows a smoothed scan of data. The peak cathodic current and the extrapolated baseline for this peak are also shown.

II. SWY-1 STUDIES

II.1. Determination of Optimal Time for Sampling

The first step in using the new system was determination of the time for equilibration within the clay film. To do this, an experiment was conducted to determine the time for equilibration in response to changing electrolyte concentrations. The ratio ($R=I_{pcme}/I_{pbare}$) was determined in a series of electrolytes where 8 minute, 30 minute, and 45 minute equilibration timed were employed. Figure 18 shows that a 45 minute equilibration period is necessary to ensure complete expansion of the clay film. At the lower equilibration times, the clay film appeared to continue its expansion in the increasingly concentrated electrolyte solutions. Since this is unlikely, it is assumed that the clay film had not fully equilibrated in the low electrolyte concentration prior to the solution change. Therefore, it continued this equilibration process in the high electrolyte concentration and the clay appeared to continue swelling. In order to avoid this effect, a 45 minute equilibration period was used in all subsequent studies.

II.2 Comparison to Previous Results

Additionally, the system must be shown to give results consistent with previous work. A standard experiment in our laboratory is to determine the effect of decreasing NaCl concentrations on the ratioed current. To confirm that the results from the new system are comparable to those from a previous experiment, the results from the two types of experiments were compared. As can be seen from Figure 19, the new experimental setup gives results similar to the previous experimental method. The lower

Figure 18: Effect of time on swelling of SWy-1 clay films in decreasing then increasing NaCl concentrations. Experimental conditions are 35 μg clay, 2 mM $Fe(CN)_6^{3-}$, 500 mV/s scan rate.

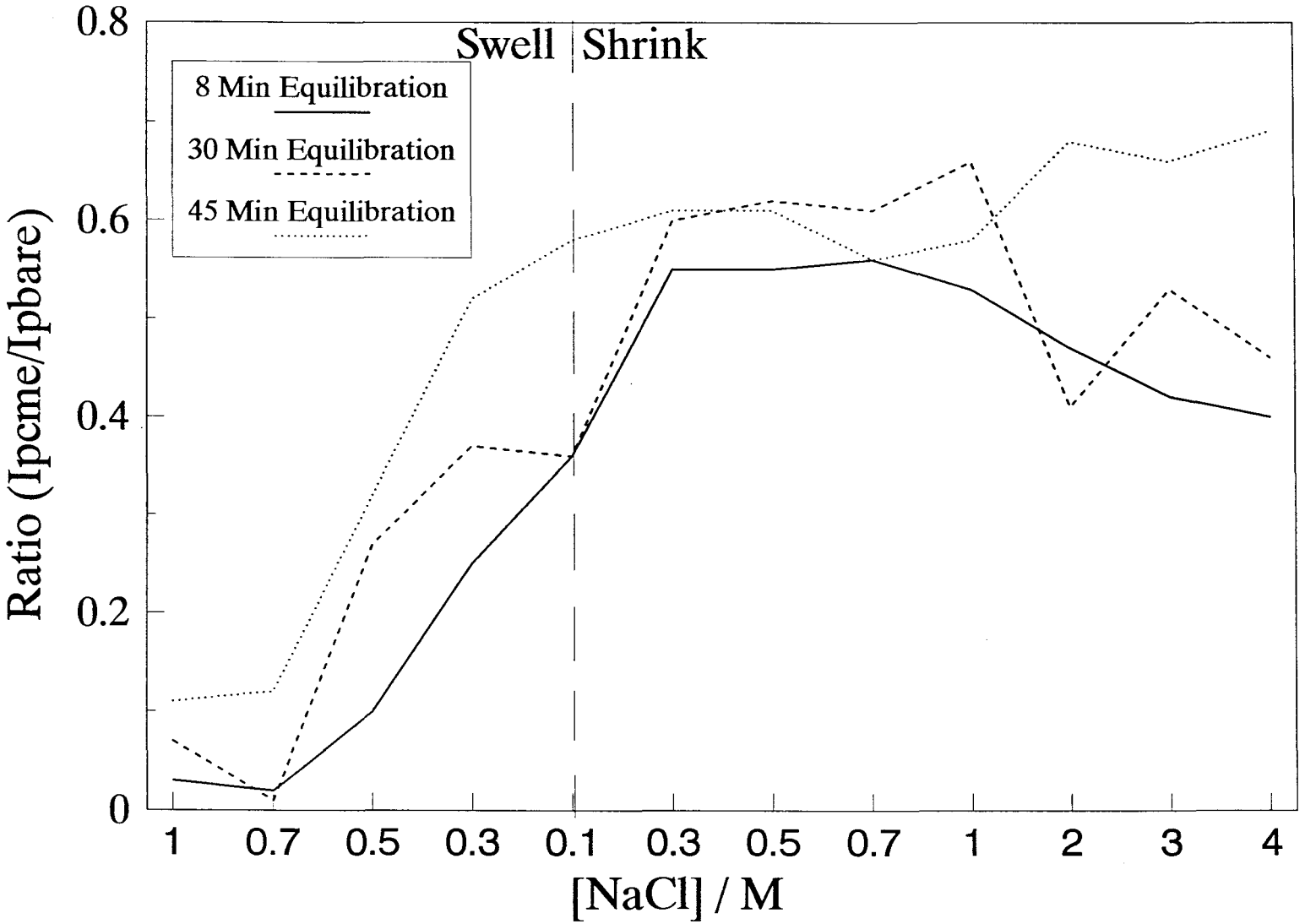
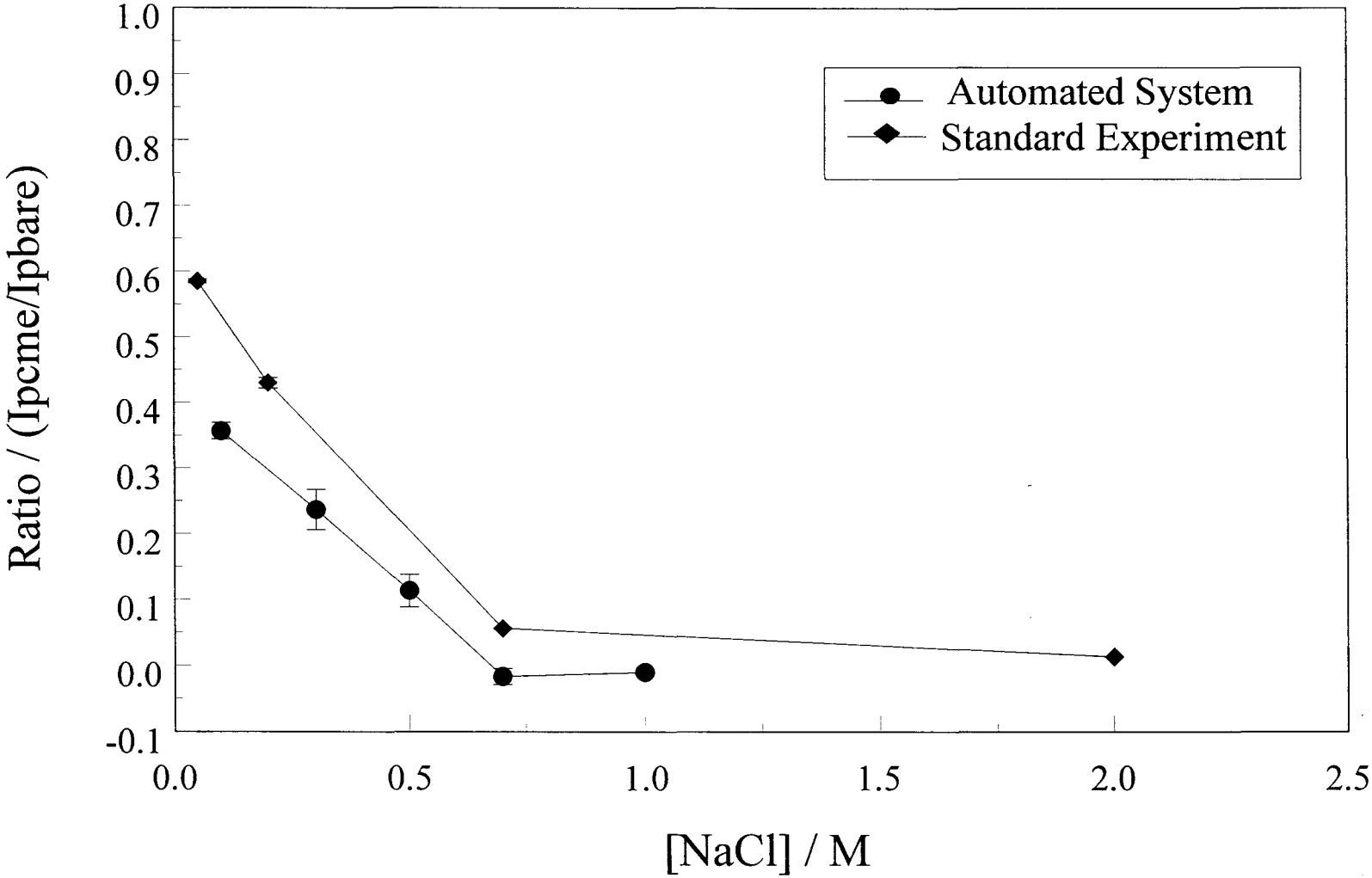

Swell
Shrink
8 Min Equilibration
30 Min Equilibration
45 Min Equilibration
Ratio (Ipcme/Ipbare)
0.8
0.6
0.4
0.2
0
1
0.7
0.5
0.3
0.1
0.3
0.5
0.7
1
2
3
4
[NaCl] / M

Figure 19: Comparison of ratioed current as a function of electrolyte concentration for two types of experiments. Automated system represents current experimental system. Experimental conditions are 35 μg clay, 2 mM $Fe(CN)_6^{3-}$, 500 mV/s scan rate, 45 minute equilibration period. Each curve represents the average of three separate clay films. Standard experiment represents previous experimental method. Experimental conditions are 35 μg clay, 2mM $Fe(CN)_6^{3-}$, 50 mV/s scan rate, 10 minute equilibration period. Each data point represents the average of three separate clay films.


Automated System
Standard Experiment
Ratio / (Ipcme/Ipbare)
[NaCl] / M
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
0.0
0.5
1.0
1.5
2.0
2.5

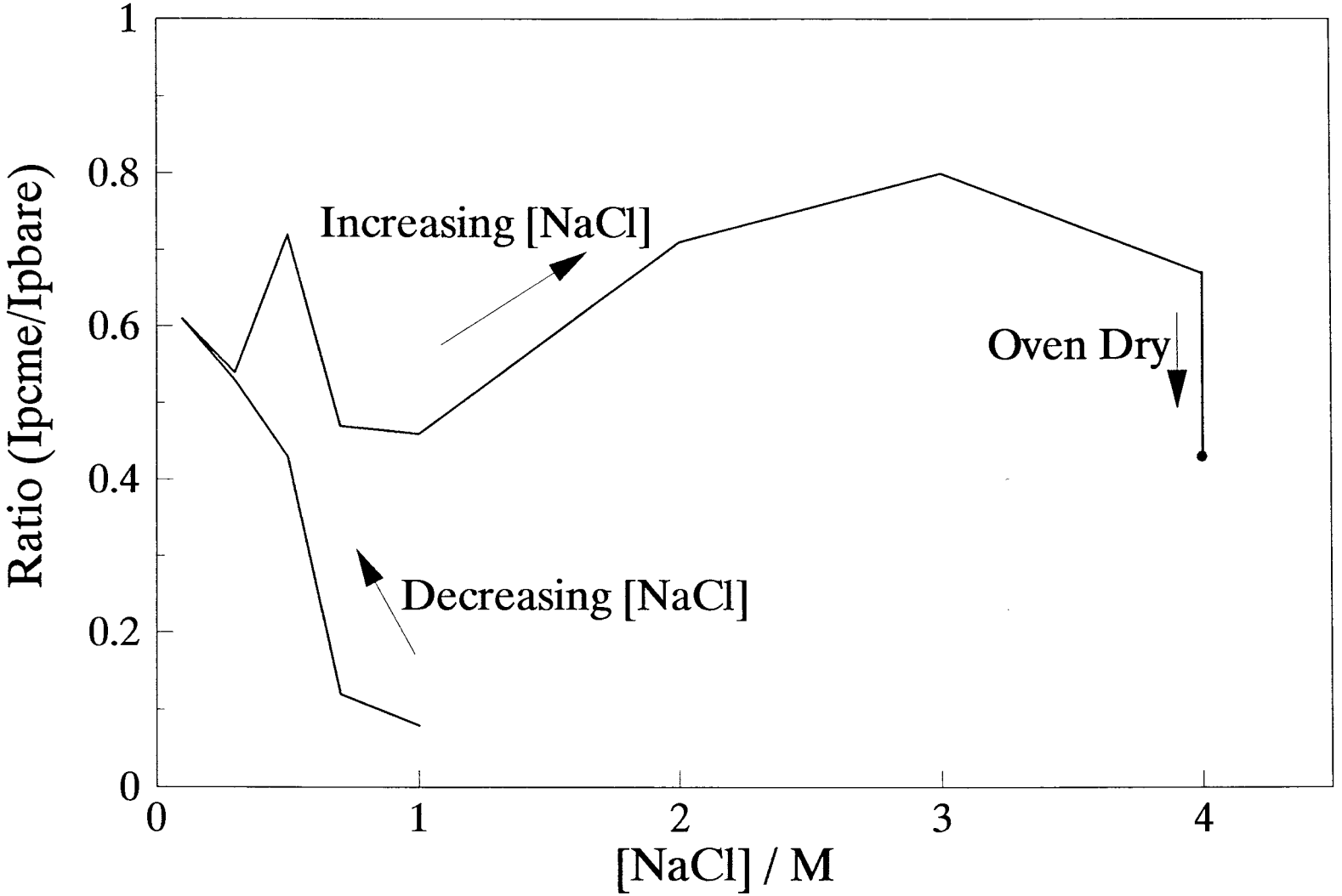
ratio values seen with the new system are most likely due to the longer equilibration time used in the current method. While the longer time period gives the film more time to swell fully, it also allows rearrangements to occur within the clay structure that can lead to a decrease in the porosity of the clay film.

In this experiment, the results from three clay films were averaged. This procedure was followed in all studies that investigated the effect of electrolyte concentration on the interlayer spacing in the clay film. In experiments where the processes that were involved in reaching the final interlayer spacing are of primary concern, the results from a single clay film are presented. In these experiments, each clay film gave slightly different results. Averaging these results would obscure the true nature of the process. Therefore, a representative, rather then an averaged result is presented.

II.3 Swelling and Shrinking Curves

One of the primary advantages of the new system is the ability to follow the response of a single clay film to changing electrolyte conditions. In a typical experiment, a single clay film is exposed to increasingly dilute then to increasingly concentrated electrolyte solutions. The results for this experiment are shown in Figure 20. Once again, the initial swelling results correspond to those of previous studies. The results for the portion of the experiment where the clay film is exposed to increasingly concentrated NaCl are surprising. These results indicate that once a clay film is swollen, the

Figure 20: Ratioed current as a function of electrolyte concentration for a single clay film. Experimental conditions are 35 μg clay, 2 mM $Fe(CN)_6^{3-}$, 500 mV/s scan rate, 45 minute equilibration period.


Ratio (Ipcme/Ipbare)
1
0.8
0.6
0.4
0.2
0
0
1
2
3
4
[NaCl] / M
Increasing [NaCl]
Decreasing [NaCl]
Oven Dry

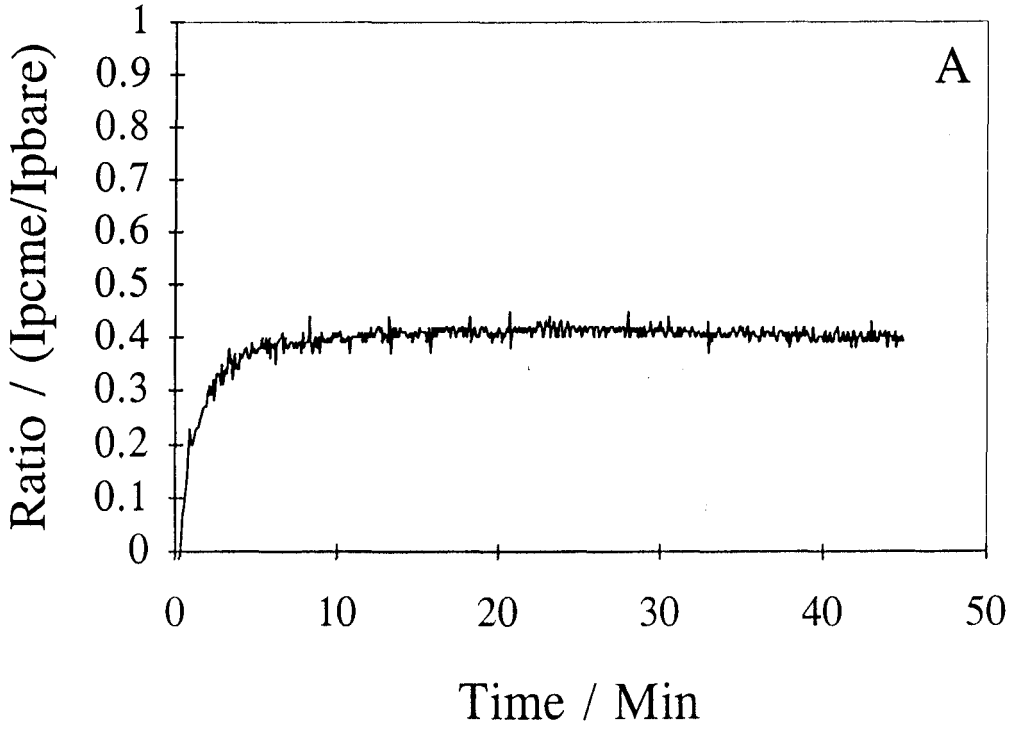
interlayer region will not collapse to the original, dry, interlayer spacing. Neither a high electrolyte concentration, nor oven drying causes the clay film to collapse.

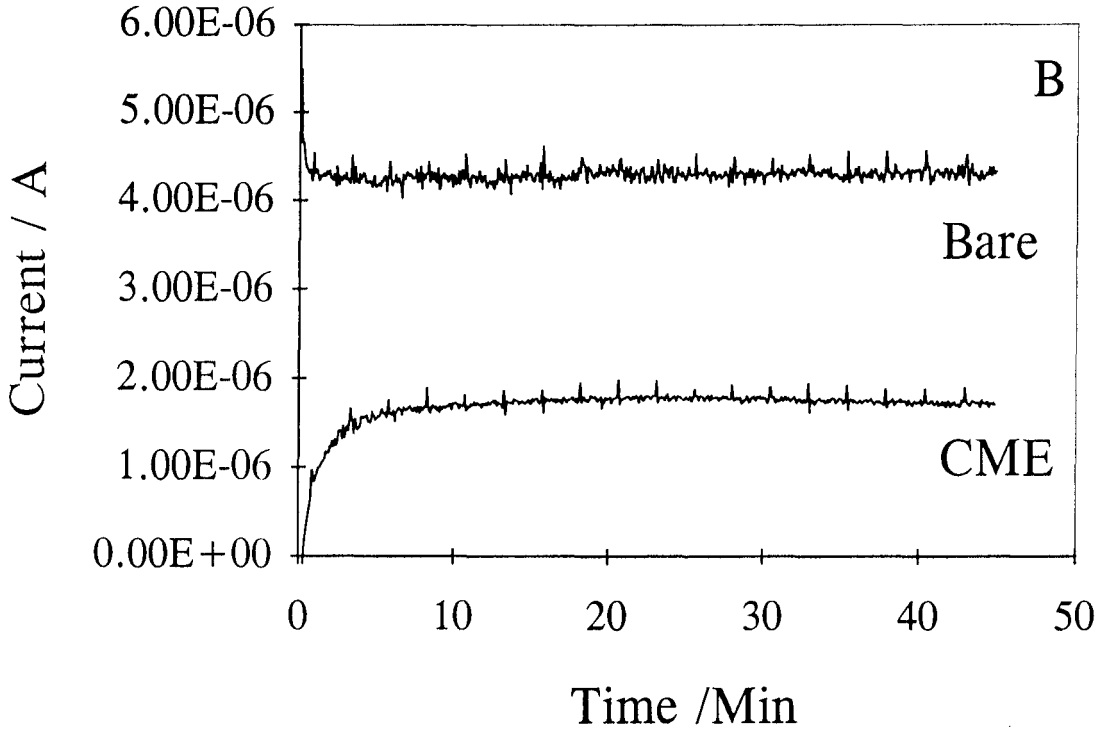
These results are consistent with other experiments where hysterisis within the clay film was observed.[16,24,64] The explanation for this phenomena concerns the organization of the clay platelets within the clay film.[37,52] When the experiment begins, the clay platelets are in a collapsed turbostatic state. This means that while they are aligned parallel to the electrode surface, there is random rotation around the z or stack axis. When the clay film is placed in solution, water enters the interlayer region between the clay platelets. This causes the clay structure to expand. Rearrangement of the platelets occurs relative to one another in order to best accommodate the interlayer water molecules. This results in rotation around the z axis. When water is removed from the system the platelets collapse but they do not rearrange. Consequently, the original structure is not reobtained and hysterisis is observed.

II.4 Time Resolved Studies

Another advantage of the computerized system is the ability to follow the swelling of the clay film with time. In Figure 21, an example of the data obtained for a time resolved experiment is presented. In this experiment, a clay film that was equilibrated in 4 M NaCl is transferred to a 0.1 M NaCl solution. Equilibrating the clay film in 4 M NaCl does not expand the interlayer spacing within the clay film. Therefore, when the clay film is transferred from this electrolyte into a low electrolyte concentration, the interlayer region expands from a collapsed regime to an expanded interlayer spacing.

Figure 21: Current as a function of time. A) The ratioed current ($R = I_{pcme}/I_{pbare}$). B) The individual currents for the bare and the clay-modified electrodes. Experimental conditions are 35 μg clay, 0.1 M NaCl, 2 mM $Fe(CN)_6^{3-}$, 500 mV/s scan rate. The electrodes were previously equilibrated in 4 M NaCl for 45 minutes.


A
Ratio / (Ipcme/Ipbare)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
Time / Min


B
Bare
CME
Current / A
6.00E-06
5.00E-06
4.00E-06
3.00E-06
2.00E-06
1.00E-06
0.00E+00
0
10
20
30
40
50
Time /Min

In Figure 21A, the ratioed current for this experiment is shown. Figure 21B, shows the currents obtained at the bare and the clay-modified electrodes. As can be seen, the change in the ratioed current mirrors the change in the CME current. The results from the above experiment demonstrate that the expansion in the interlayer spacing of the clay film from a collapsed film to an expanded clay film can now be followed with time. They also indicate that exposure to a concentrated electrolyte does not prevent the swelling response of the clay film. Additionally, the results indicate that the transition from a collapsed regime to an expanded regime is a smooth transition for SWy-1.

In an opposite experiment, the response of a swollen clay film to a concentrated electrolyte solution is monitored. In this experiment, a dry clay film is equilibrated in 0.1 M NaCl then transferred to a 4 M NaCl solution. The temporal response of the clay film is shown in Figure 22. The consistent ratio value with time illustrates that the concentrated electrolyte has no effect on the swollen clay film.

In an attempt to collapse the swollen clay film, the clay film was exposed to a concentrated KCl solution. Previous work,[13,65] has shown that SWy-1 will not swell in KCl. It is therefore postulated that the presence of a large concentration of potassium ions in the system will collapse the expanded clay layers. In Figure 23, the results for an experiment where a dry clay film was equilibrated in 0.1 M NaCl then transferred to 4 M KCl are shown. While the swollen clay film did collapse, it took many hours to do so.

Figure 22: Ratioed current as a function of time. Experimental conditions are 35 μg clay, 4 M NaCl, 2 mM $Fe(CN)_6^{3-}$, 500 mV/s scan rate. The electrodes were previously equilibrated in 0.1 M NaCl for 45 minutes.

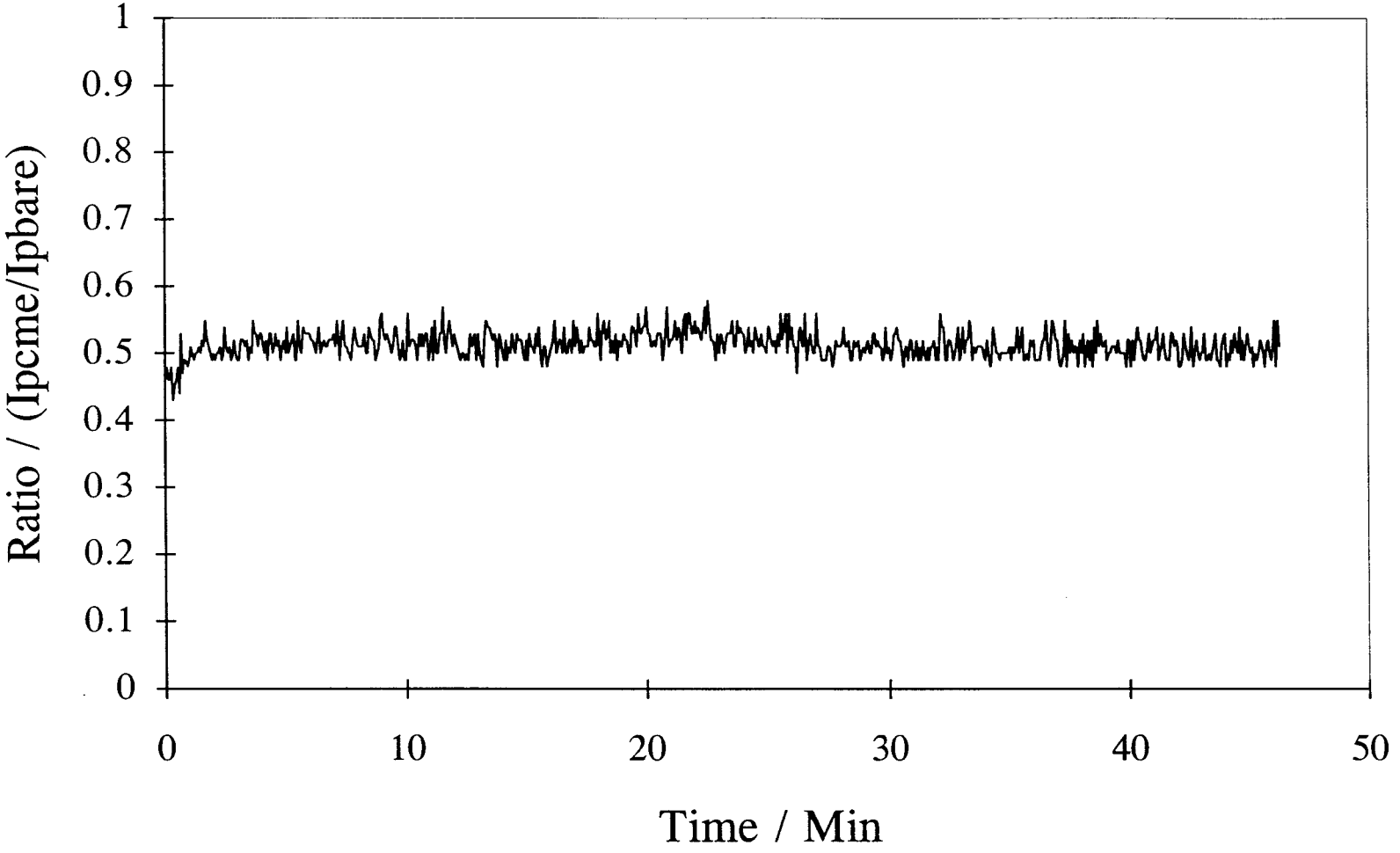
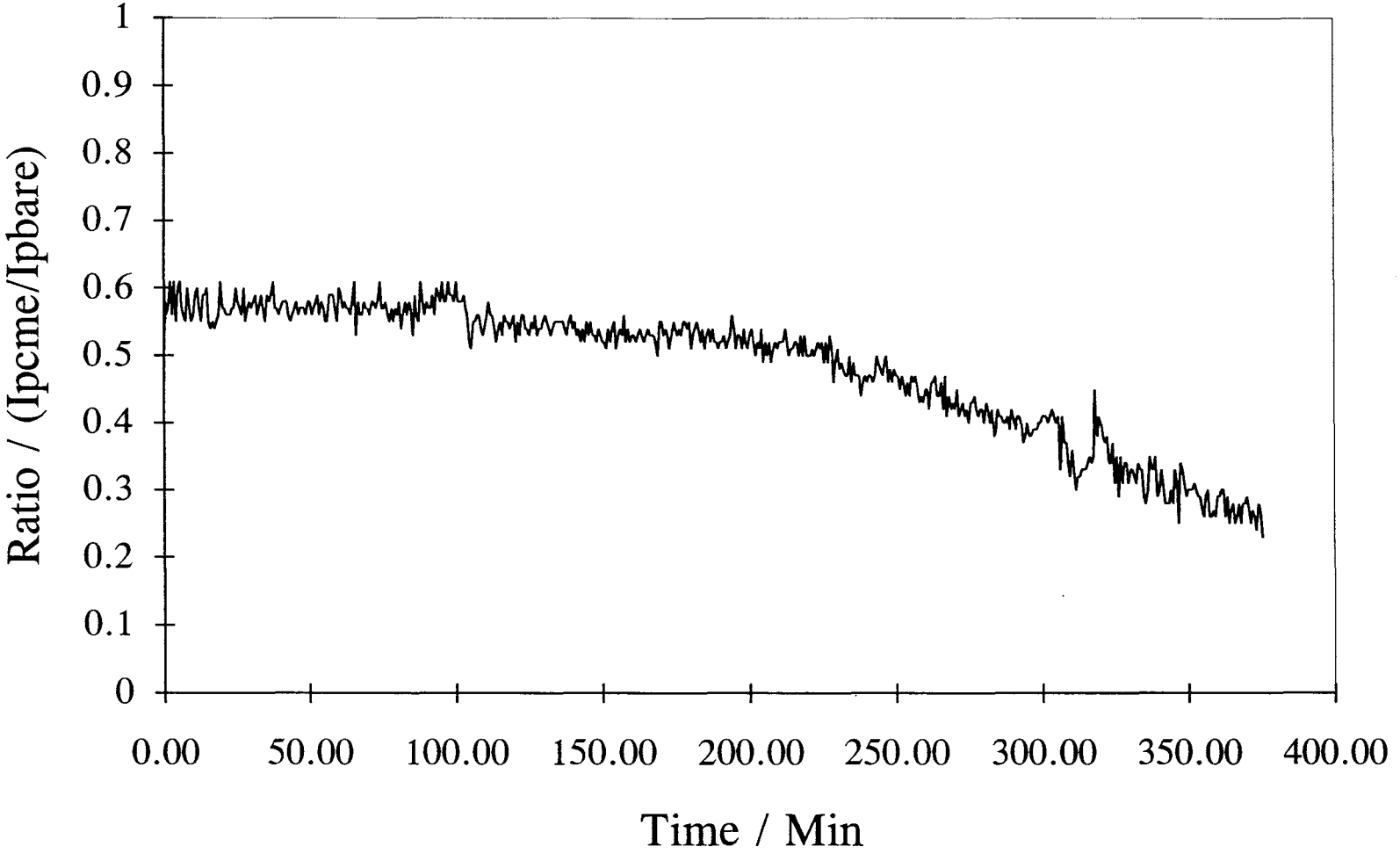

Ratio / (Ipcme/Ipbare)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
Time / Min

Figure 23: Ratioed current as a function of time. Experimental conditions are 35 μg clay, 4 M KCl, 2 mM $Fe(CN)_6^{3-}$, 500 mV/s scan rate. The electrodes were previously equilibrated in 0.1 M NaCl for 45 minutes.


Ratio / (Ipcme/Ipbare)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.00
50.00
100.00
150.00
200.00
250.00
300.00
350.00
400.00
Time / Min

In the above experiment, the exchange of the sodium cations for the potassium cations in the interlayer region followed by the rearrangement of the clay layers and their subsequent collapse is followed. A large concentration gradient and favorable exchange kinetics due to the lower dehydration energy for the potassium ions as compared to the sodium ions exists in the system.[13] Therefore, it is probably the rearrangement of the clay layers rather then the cation exchange process that is responsible for the long time period seen in the experiment. The rearrangement of the clay layers in response to K^+ has been studied by X-Ray diffraction methods and similar results have been seen.[10] Soil scientists also study similar phenomena in illites, which they term "K-fixation". They find a selectivity factor for K^+ five times greater then that for Na^+. They also find that the insertion of potassium leads to irreversible changes in the geometry of the clay lattice.[66] The present results indicate that the new system offers an easy and rapid way to study this same phenomena.

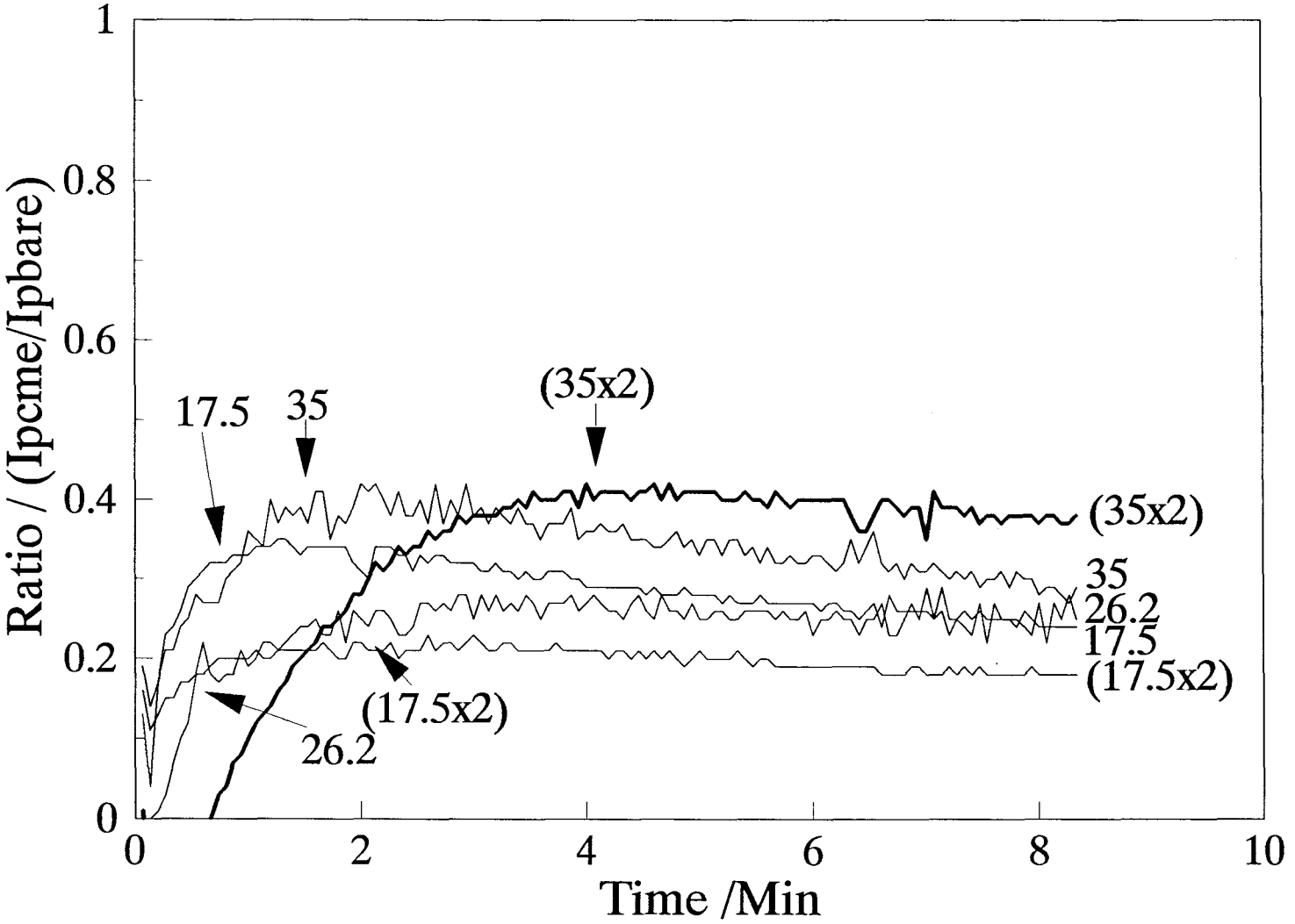
II.5. Effect of Clay Film Thickness

The effect of the thickness of the clay film on the time resolved swelling of the SWy-1 clay film was examined. It was postulated that a thicker clay film would result in a longer time for penetration of the electrolyte solution. This could then, in turn, affect the time for swelling or even the shape of the swell curve. If this were indeed the case, then any conclusions made for the clay film would be dependent on the thickness of the clay film.

To investigate the effect of clay film thickness, a series of solutions with different concentrations of clay were formed and clay films were prepared from these solutions. Previous research has shown that the most concentrated clay solution possible is 35 g/L. Above this concentration, the SWy-1 solution forms a thick gel and cannot be used. To obtain a clay film with a clay concentration greater then 35 μg, two 1 μl drops of a 35 g/L solution were successively applied and dried on the electrode. As a control for this experiment, a 35 μg clay film was prepared from 2 drops of a 17.5 g/L clay solution. The diameter of the drops was monitored for the different clay films as a means of gauging the thickness of the clay film. No appreciable differences in diameter were observed. Therefore, it can safely be assumed that as the amount of clay applied to the electrode is changed, the thickness of the clay film is changed.

The results from this study are presented in Figure 24. While the 70 μg clay film appeared to have a slightly slower swelling response then the other films, the differences were by no means significant. These results indicate that the swelling response is controlled by the clay rather then by the thickness of the clay film. In nature, there would certainly be a delay period in the time for diffusion due to thickness of the clay bed. The results from our experiments do not access these effects. Instead, our experiments examine the nature of the swelling process in the clay itself and it's effect on the diffusional properties of the overall clay film.

Figure 24: Effect of clay film thickness on the temporal swelling of SWy-1 clay film. Experimental conditions are 0.1 M NaCl, 2 mM $Fe(CN)_6^{3-}$, 500 mV/s scan rate. The concentration of clay in the clay film is indicated on the graph.


Ratio / (Ipcme/Ipbare)
Time /Min
0
0.2
0.4
0.6
0.8
1
0
2
4
6
8
10
17.5
35
(35x2)
26.2
(17.5x2)
(35x2)
35
26.2
17.5
(17.5x2)

II.6. Temperature Studies

To better understand the nature of the interlayer expansion, the temporal response of the clay film to a low electrolyte concentration was monitored at several different temperatures. In these experiments, a dry clay film was placed directly into a 0.1 M NaCl solution that was previously equilibrated at the given temperature.

The effect of temperature on time for swelling and on the final interlayer spacing was studied. The effect of temperature on the final interlayer spacing is graphed in Figure 25. Double layer theory states that the double layer will vary with $T^{1/2}$.[67] The present results indicate no temperature dependence in the present clay system. Therefore, double layer theory has no relevance in predicting the temperature dependence of the final interlayer spacing in this instance. These results are consistent with results obtained by Zhang et al., who measured the interlayer spacing directly via X-Ray diffraction.[35] They also found no dependence on temperature for the interlayer spacing in a clay film.

The temporal response of the clay as a function of temperature was also monitored. These results are presented in Figure 26. While the final interlayer spacing was invariant, temperature definitely affects the initial swelling curves. While it appears that the rise time of the curve is steeper with increasing temperature, these results are somewhat questionable due to the presence of water within the electrochemical cell at the higher temperatures. This water is attributed to the condensation of humidity in the laboratory atmosphere during temperature equilibration

Figure 25: Effect of temperature on the final interlayer spacing. Experimental conditions are 35 μg clay, 0.1 M NaCl, 2 mM $Fe(CN)_6^{3-}$, 500 mV/s scan rate, 45 minute equilibration period. Results are average of 10 replicates.

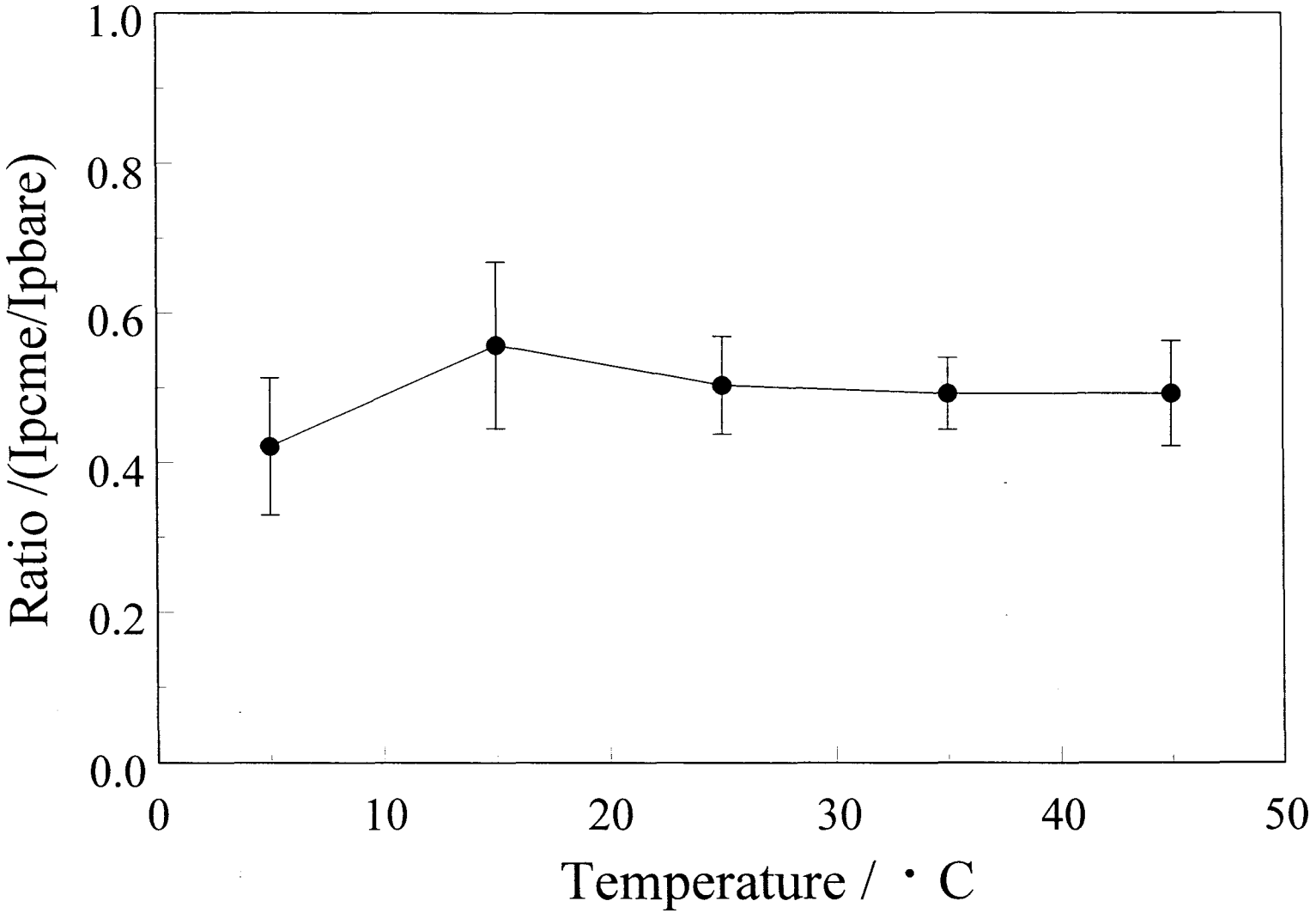
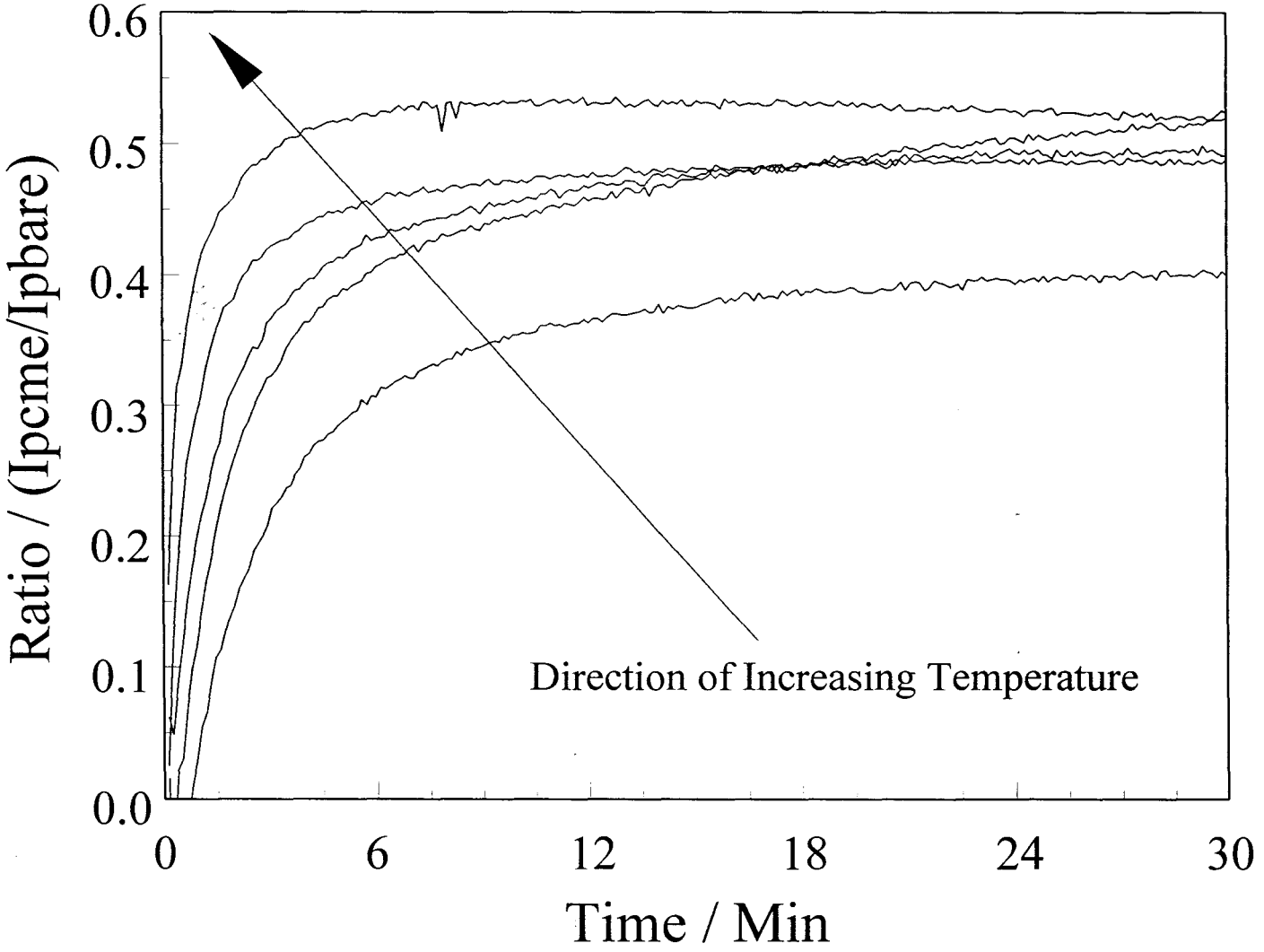

1.0
0.8
0.6
0.4
0.2
0.0
Ratio /(Ipcme/Ipbare)
0
10
20
30
40
50
Temperature / ・C

Figure 26: Current as a function of time for 5 temperatures. Temperatures monitored were 5°C, 15°C, 25°C, 35°C, and 45°C. Curves represent the average of 10 replicates. Experimental conditions are 35 μg clay, 0.1 M NaCl, 2 mM $Fe(CN)_6^{3-}$, 500 mV/s scan rate.


0.6
0.5
0.4
0.3
0.2
0.1
0.0
Ratio / (Ipcme/Ipbare)
0
6
12
18
24
30
Time / Min
Direction of Increasing Temperature

of the electrochemical cell. In order to further explore the effects of temperature, modifications to control the effects of humidity within the system are necessary.

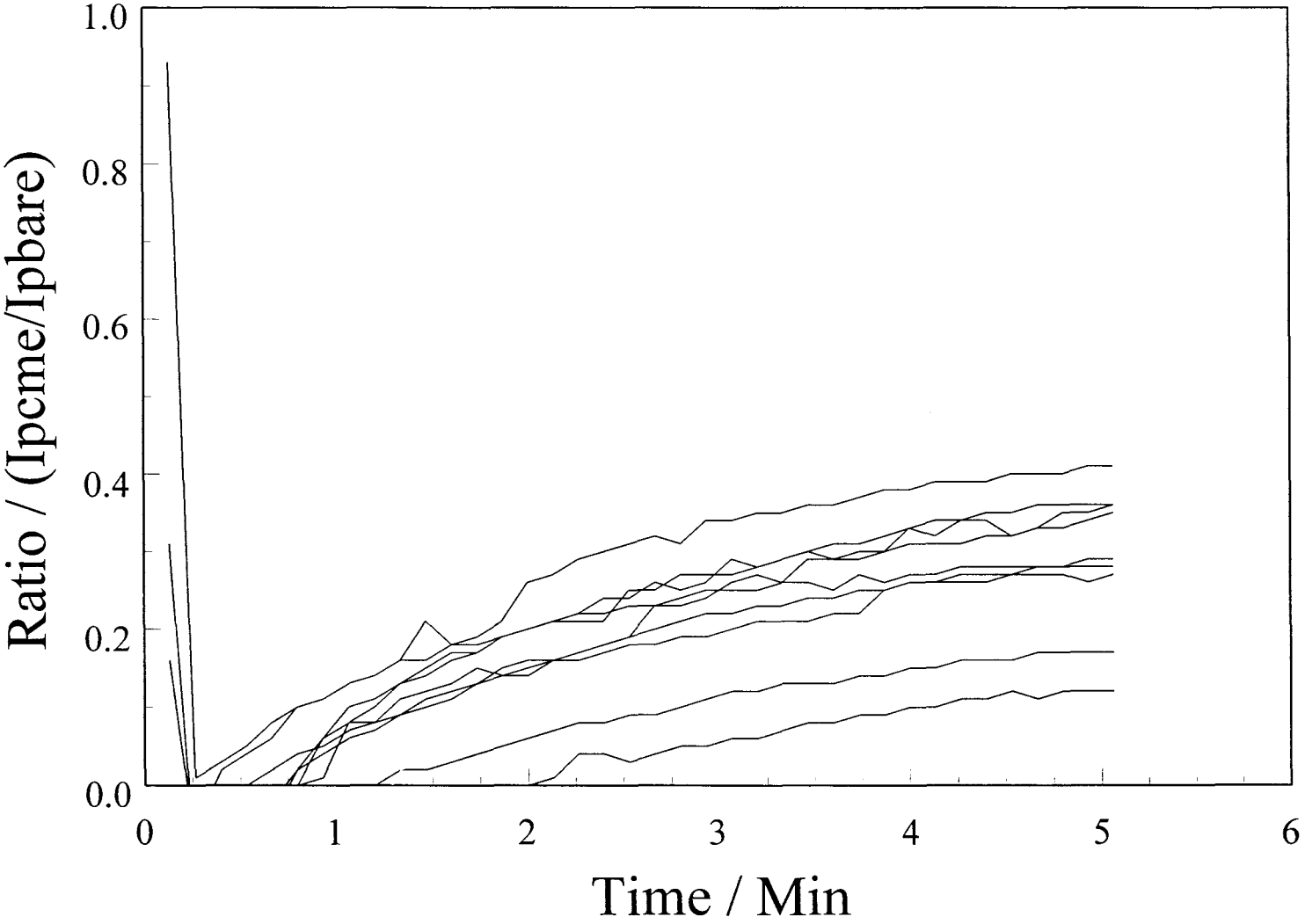
While, in general, the rise time of the curves changed with temperature, there was variability in the results. In fact, at the lower temperatures, especially in the 5°C data, the data appear to cluster (Figure 27). These results could be indicative of the presence of different energy levels associated with different hydration levels within the clay film. Recent theory and experiments suggest that swelling occurs in epitaxial layers of water with large energy barriers between the formation of the different water layers.[18,27,36,48,68] When the clay starts from the dry state there are different energy levels associated with the structure of the clay sheets and the structure of the water present in the system.[31] Present results indicate that these energy levels may be quantized. This phenomena appears to be accessible to exploration through the use of the present system.

III. Survey of Clay Types

The experiments with SWy-1 show the utility of the system for examining the response of a clay film to different environmental conditions. In nature, not only are there different environmental conditions, but there are also a variety of clays present in the clay system. Very seldom is a single homogeneous clay present in a true natural environment. For this reason, a study on the affects of different clays on the diffusional properties of clay-modified electrodes was undertaken.

Before proceeding to the experiments with mixed clay systems, it was necessary to survey the response of individual clays. While the diffusional properties and the

Figure 27: Temporal swelling of SWy-1 at 5°C. Experimental conditions are 35 μg clay, 0.1 M NaCl, 2 mM $Fe(CN)_6^{3-}$, 500 mV/s scan rate.


1.0
0.8
0.6
0.4
0.2
0.0
Ratio / (Ipcme/Ipbare)
0
1
2
3
4
5
6
Time / Min

factors that effect these properties for SWy-1 are well understood, this is not the case with other clays. For this reason, the response of a series of clays to two different sets of experiments was examined. The clays that were evaluated are shown in Figure 28. The experiments that were performed for each clay were an investigation of the time resolved swelling of the clay and an investigation of the affect of decreasing electrolyte concentration. As with the SWy-1 experiments, the temporal response of the clay yields information on the nature of the swelling process in the clay. The electrolyte studies examine the overall swelling of the clay. Combining the results for these two studies provides a way of distinctly defining the influence of each clay type in a mixture of clays.

Each clay type will uniquely influence the diffusional properties of a clay film. In general, two paths for diffusion will exist in a clay film. The first path will be diffusion through defects in the clay particle alignment or diffusion around the clay particles. The second path will be diffusion through the region between the clay layers. The predominance of one pathway over another in the clay film will depend upon the types of clays present, the organization of the clay film, and the interlayer spacing in the swelling clays. In the non-swelling clays the first pathway will dominate while, in the swelling clays, the second pathway will dominate. In some materials, the presence of both types of diffusion should be discernable. Additionally, the effect of the organization of the clay film and the effect of the interlayer spacing need to be considered. If the clay film is not well organized, there will be defects in the particle arrangement. These cracks will result in an inability to distinguish the swelling clays from the non-swelling

Figure 28: Clays evaluated in individual clay experiments. All information is from CMS chemical analysis.[69] Formulas were calculated from CMS chemical analysis. A unit charge of 44 was assumed for all clays except KGa-1. For KGa-1 a unit charge of 24 was assumed. The analysis of SHCa-1 indicated the prescence of a large amount of carbonate. This was incorporated into the analysis.

Clay Type	Clay Name	Location	Formula	CEC (meq/g)
SWy-1	Montmotillonite	Wyoming	$(Si_8)(Al_{2.93}Fe^{3+}_{0.32}Fe^{2+}_{0.03}Mg_{0.58})O_{20}(OH)_4$	76.4
STx-1	White Montmorillonite	Gonzales, TX	$(Si_8)(Al_{2.3}Si_{0.67}Fe^{3+}_{0.06}Mg_{0.21})O_{20}(OH)_4$	84.4
SAz-1	Calcium Montmorillonite	Cheto, AZ	$(Si_{7.96}Al_{.02})(Al_{2.73}Fe^{3+}_{0.14}Mg_{1.27})O_{20}(OH)_4$	120
SHCa-1	Trioctahedral Lithium Montmoillonite	California	$(Si_{7.67}Al_{0.18})(Mg_{5.04}Li_{1.94})O_{20}(OH)_4$	43.9
KGa-1	Well Crystallized Kaolinte	Georgia	$(Si_{3.8}Al_{0.07}Ti_{0.1})(Al_{3.99}Fe_{0.01})O_{10}(OH)_8$	2

clays. To prevent this from occurring, the clay is spin coated onto the electrode surface. This results in a well organized clay film. Finally, in the swelling clays, the effect of the interlayer spacing needs to be considered. If the clay film is thoroughly swollen, then diffusion will be rapid. This diffusion must, however, be distinguished from the rapid diffusion seen through fissures in the clay film. Figure 29 graphically illustrates all these possible pathways for diffusion of an anion through a clay film.

III.1 Time Resolved Studies

In these experiments, the temporal swelling of the individual clays was examined. A dry clay film was placed into a 0.1 M NaCl solution and the response of the clay film was monitored over time. Comparing the results for the different clay films yields information on the type of diffusion that occurs in the clay and on the process of interlayer expansion.

The temporal swelling of a representative clay film for each clay type is presented in Figure 30. These results show that the processes involved in the interlayer expansion are different in the different clays. The KGa-1, STx-1 and SAz-1 all exhibit an immediate, unchanging current when placed into the low electrolyte solution. The magnitude of this current is, however, different in each instance. The SWy-1 and SHCa-1 both exhibit a slowly developing current. Once again, the final magnitude of these two currents is different.

Figure 29: Effect of clay type, clay film organization, and interlayer spacing on the diffusion of an anion through a clay film. In the figure, the filled rectangles indicated a non-swelling clay while the non-filled rectangles indicate a swelling clay.

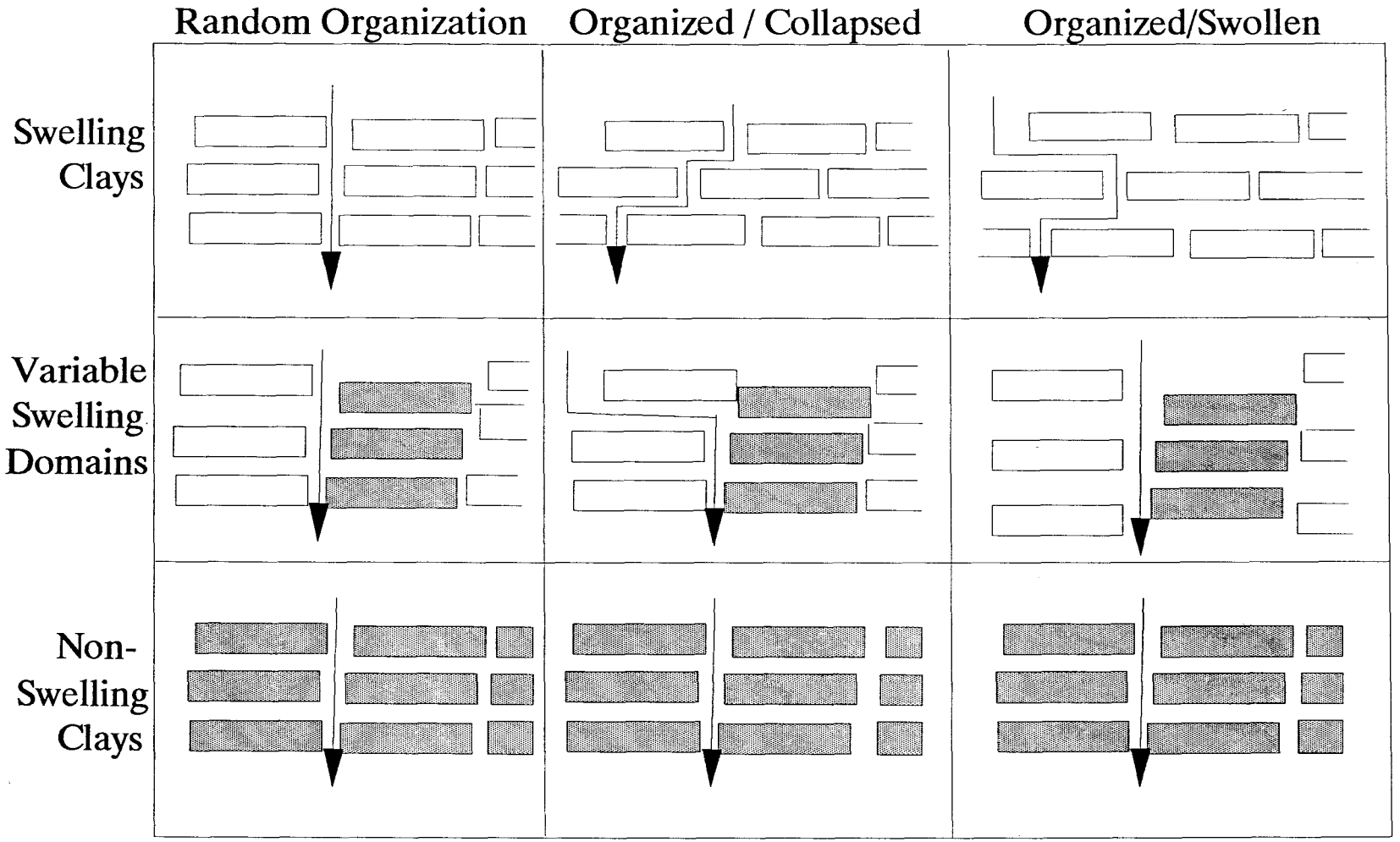
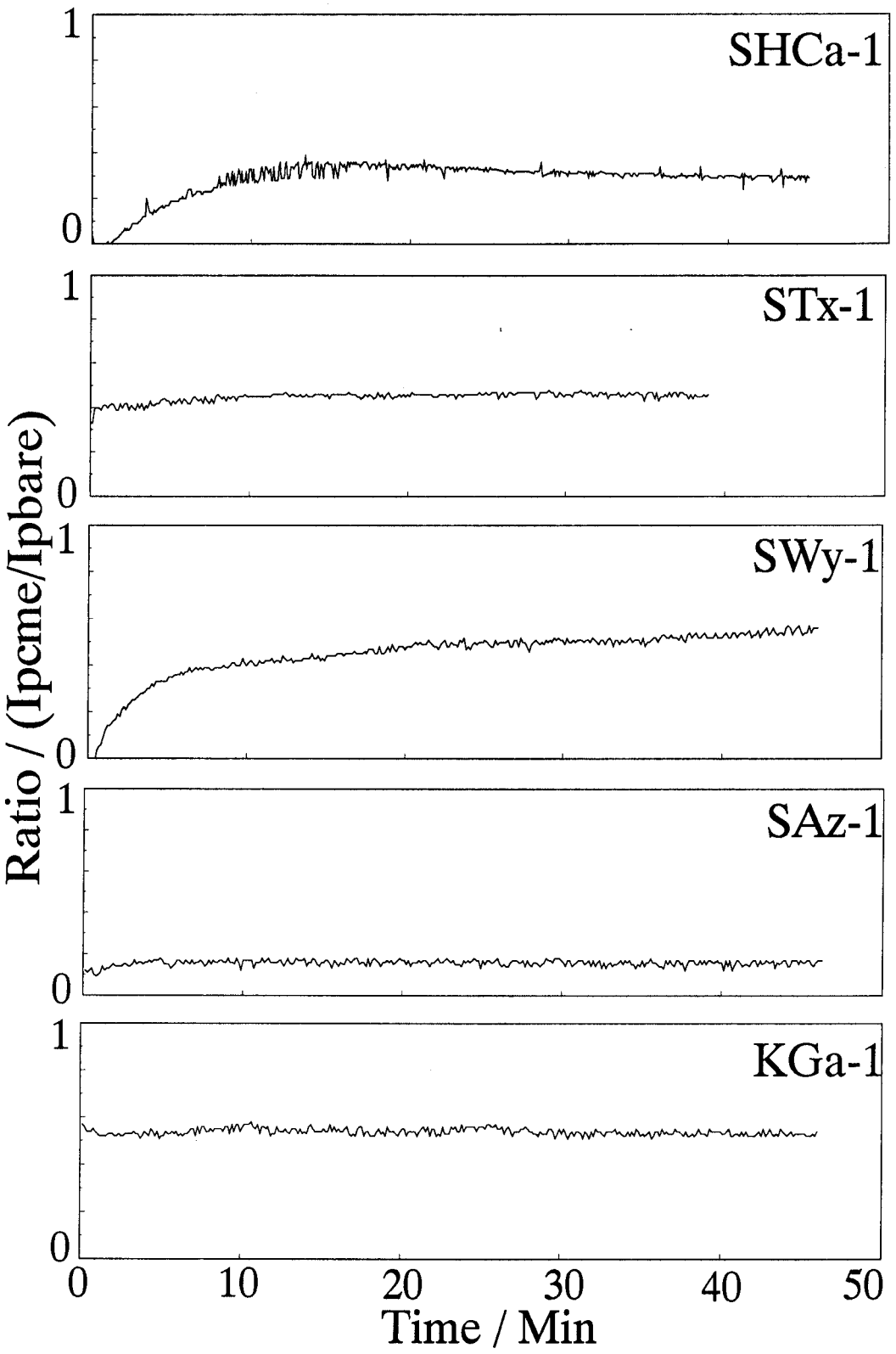

Random Organization
Organized / Collapsed
Organized/Swollen
Swelling Clays
Variable Swelling Domains
Non-Swelling Clays

Figure 30: Temporal swelling of individual clays. Experimental conditions are 35 μg clay, 0.1 M NaCl, 2 mM $Fe(CN)_6^{3-}$, 500 mV/s scan rate.


SHCa-1
STx-1
SWy-1
SAz-1
KGa-1
1
0
Ratio / (Ipcme/Ipbare)
0
10
20
30
40
50
Time / Min

III.1.2 Swelling Curves

These experiments examined the response of the clay films to a series of electrolyte concentrations. In this set of experiments, it is the final, equilibrium spacing in each electrolyte that is of concern. This yields information on the effect of electrolyte on the swelling nature of the clay film.

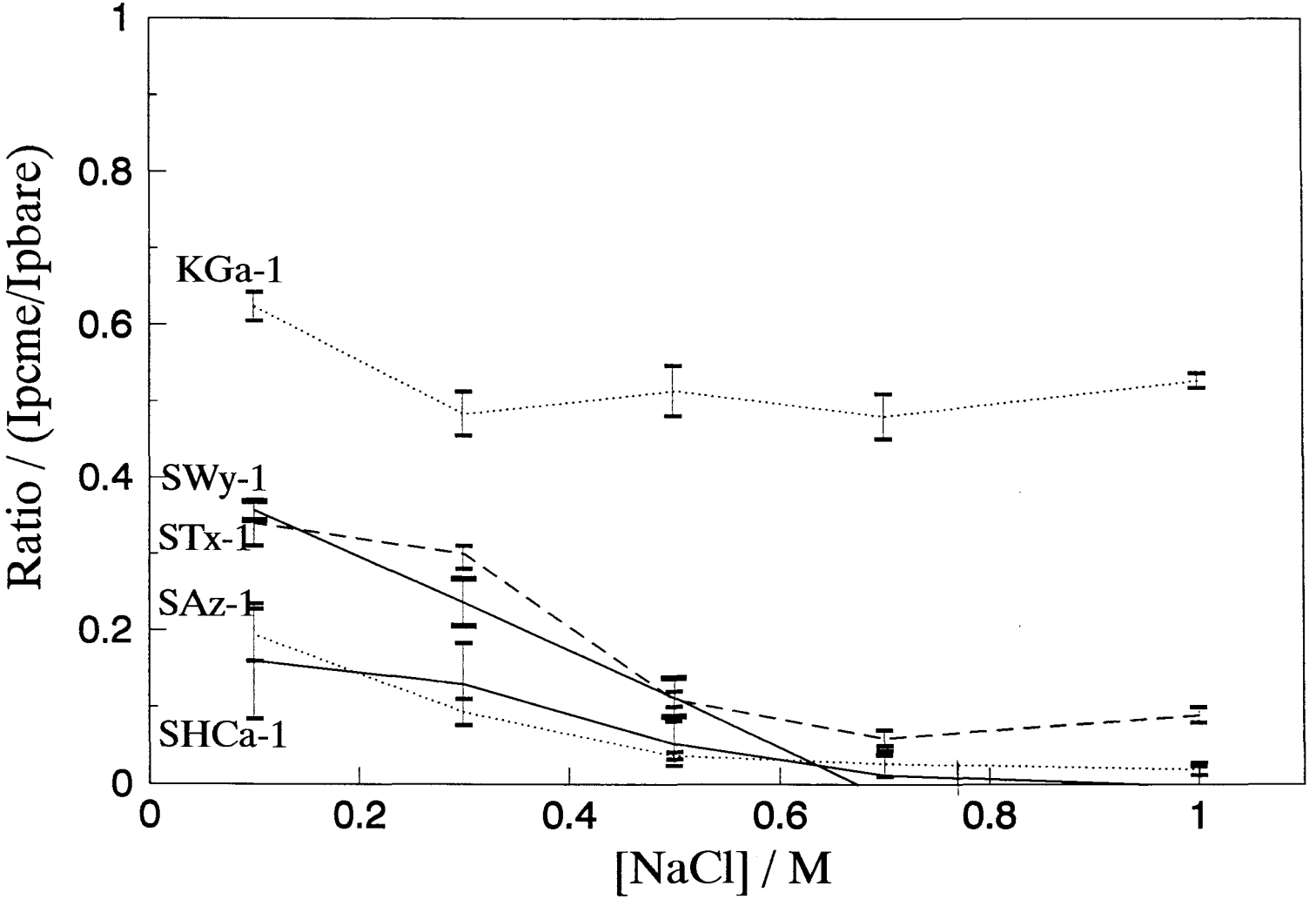
Figure 31 shows the averaged results for the different clay types. From this graph it is evident that the clays fall into three groups. All of the swelling clays exhibit electrolyte dependence while the KGa-1 does not. Within the swelling clays, the SAz-1 and the SHCa-1 both swell to a ratio current near 0.2. The SWy-1 and the STx-1 exhibit greater swelling in the lower electrolyte concentrations. They swell to a final ratioed current value of 0.4.

III.3 Effect of Clay Type on the Diffusional Properties of $Fe(CN)_6^{3-}$

III.3.1 2:1 Layer Clays

The STx-1, SAz-1, SWy-1 and SHCa-1 are all swelling 2:1 layer clays. The differences in the shape of the swelling curves indicate differences in the swelling processes. For the STx-1 and the SAz-1, an immediate current is seen while, for the SHCA-1 and the SWy-1 the current develops gradually. The final ratiod current value also yields important information on the clay. For the SHCa-1 and the SAz-1, the final interlayer spacing is small while, for the SWy-1 and the STx-1 it is relatively large. Preliminary, unpublished research in this laboratory indicates that a ratioed current value

Figure 31: Effect of NaCl concentration on swelling of different clay types. Experimental conditions are 35 μg clay, 2 mM $Fe(CN)_6^{3-}$, 500 mV/s scan rate. Lines represent an average of three clay films.


Ratio / (Ipcme/Ipbare)
[NaCl] / M
KGa-1
SWy-1
STx-1
SAz-1
SHCa-1
0
0.2
0.4
0.6
0.8
1

of 0.2 corresponds to an interlayer spacing of 20Å. The initial expansion of a clay's interlayer is termed crystalline swelling and corresponds to an expansion in the interlayer to a spacing of approximately 20 Å[70]. Therefore, in the SAz-1, and in the SHCa-1, it is likely that this initial crystalline swelling is the only process that occurs in the clay film. The SWy-1, and the STx-1, however, swell to a final ratiod current value of 0.4. For these clays, the initial swelling is just part of an overall process that results in a large interlayer spacing within the clay film. For the STx-1 the transition from the crystalline to the osmotic swelling region is immediate. For the SWy-1 it is part of an overall smoothly developing process. In both these clays there are no large differences between the initial swelling and the subsequent swelling processes that occur.

The limited swelling of the SHCa-1 and the SAz-1 was surprising since they are both classified as swelling clays. For the SHCa-1, the results are attributed to the nature of the clay. SHCa-1 is a high gel forming clay with a low cation exchange capacity. DLVO theory predicts that swelling should decrease with decreasing CEC. For the SAz-1, the low swelling is attributed to incomplete exchange of the native calcium ions in the clay. SAz-1 is naturally a calcium montmorillonite and is known to not swell beyond an interlayer spacing of 20 Å[51]. Analysis of the SAz-1 for calcium content indicates 0.02% calcium present in the clay. While this is substantially less than the 1.3% present in the un-exchanged SAz-1 sample, it is still enough to raise questions about the swelling mechanisms present in the SAz-1 sample. Perhaps the small amount of calcium present in the clay sample was enough to control the response of the entire clay film. Alternatively, lower swelling results have been seen in other studies with Na^+-SAz-1.

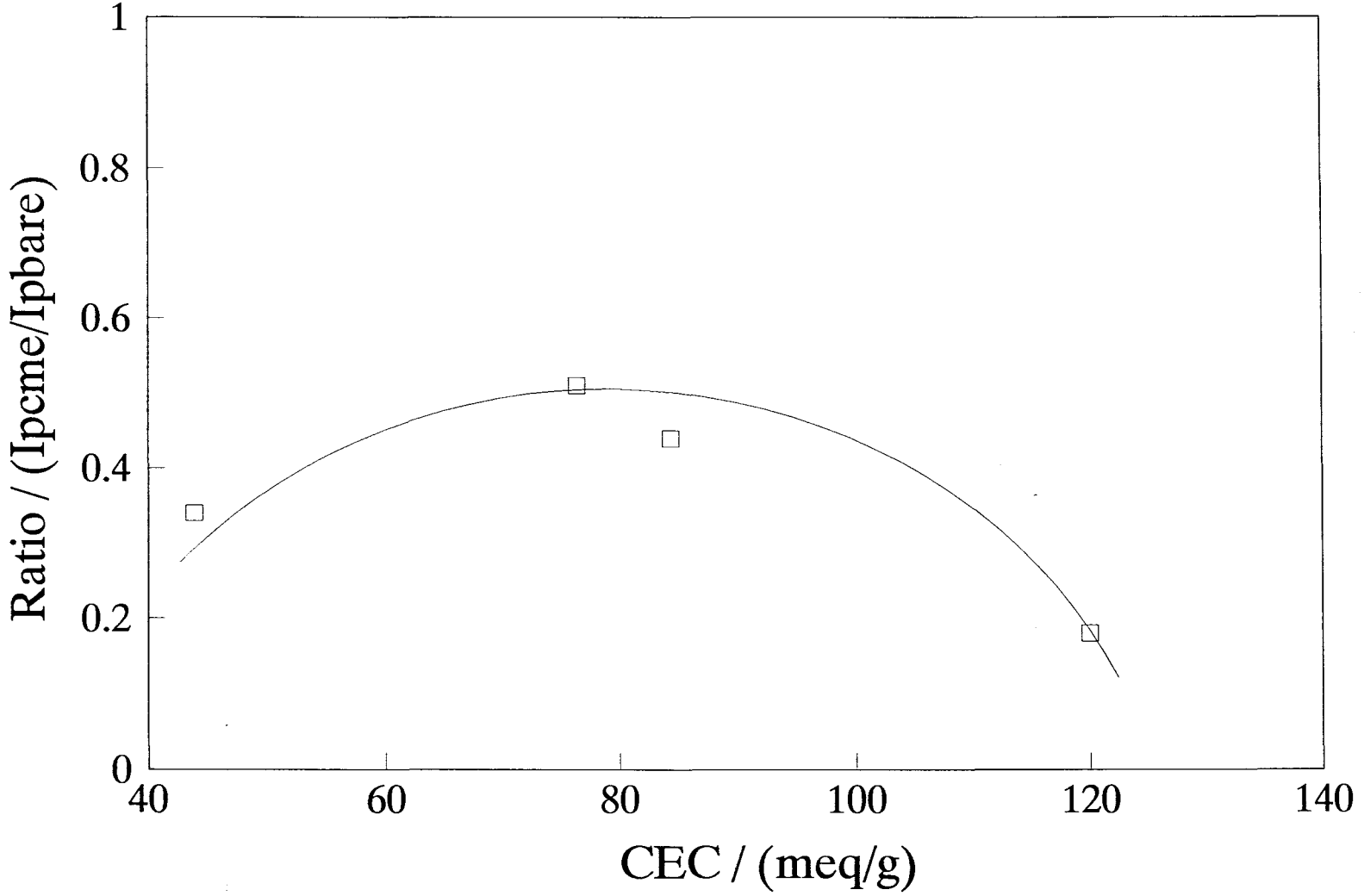
These results were attributed to the high charge on the clay, as evidenced by the high cation exchange capacity of the clay.[18] Very highly charged clays do not swell to the same extent as the intermediately charged clays due to cation pillaring.[66] Research on the valence of iron in the clay and its effect on swelling has led to the theory that there are different swelling domains in the clay structure.[20,71] Reduction of the iron in the clay leads to domains of lower swelling. In the SAz-1 there are probably domains of low swelling around either the calcium ions or the regions of cation pillaring. These domains result in the SAz-1 not swelling to the same extent as the SWy-1 sample.

In Figure 32, the final ratiod current values are plotted against the cation exchange capacity (CEC) for each of the clays. As stated, according to DLVO theory, the swelling of a clay will increase proportionally to the CEC of the clay. These results illustrate that this theory holds true for the lower charged clays. For the clays with higher charge, however, cation pillaring of the interlayer occurs and swelling decreases with increasing CEC.

III.3.2 1:1 Layer Clays

The KGa-1 is a 1:1 non-swelling kaolinite. It begins with a very small interlayer region and it does not expand this region in response to a low electrolyte concentration. Subsequently, the processes involved in the diffusion of a species through this material are very different from those involved in the montmorillonites. Since the interlayer region remains very small in the KGa-1, if the $Fe(CN)_6^{3-}$ were diffusing through this

Figure 32: Correlation between cation exchange capacity and swelling for four swelling clays. Experimental conditions are 35 μg clay, 0.1 M NaCl, 2 mM $Fe(CN)_6^{3-}$, 500 mV/s scan rate. Results represent an average of three clay films. Curve is drawn purely for illustrative purposes.


Ratio / (Ipcme/Ipbare)
1
0.8
0.6
0.4
0.2
0
40
60
80
100
120
140
CEC / (meq/g)

region, the current would be very small due to the small path for diffusion. Because the current is large and immediate, it is thought to be due to structural defects or pinholes within the clay film. These defects allow the $Fe(CN)_6^{3-}$ to diffuse directly to the electrode surface without sampling the interlayer region.

In order to prove that these pinholes are due to the KGa-1 being a 1:1 non-swelling clay, an experiment was performed with a calcined SWy-1 sample. When a clay is heated to a very high temperature (calcined) the interlayer region is collapsed irreversibly[72] and thus, does not swell. If it is the non-swelling of the KGa-1 that causes the defects in the clay film, the calcined SWy-1 should behave in a similar manner. The temporal response of a calcined SWy-1 CME is shown in Figure 33. The response to different electrolyte concentrations is shown in Figure 34. The similarity between these results and those for the KGa-1 is striking. It can, therefore, be concluded that the non-swelling of the KGa-1 is the cause of the immediate temporal response and the insensitivity to electrolyte concentration that were seen.

IV. Mixed Clay Systems

Based on the results of the previous experiments, three clays were chosen for the mixed clay studies. These clays were SWy-1, SAz-1, and KGa-1. The SWy-1 was chosen because there already exists a large database of knowledge on the material. The SAz-1 was chosen because it, like the SWy-1 is a montmorillonite. Unlike the SWy-1, the SAz-1 does not swell to a great degree. Therefore, the effect of SAz-1 in a mixture of clays should be discernable from that of SWy-1. The third clay chosen was KGa-1.

Figure 33: Ratioed current as a function of time for heat-treated SWy-1. Experimental conditions are 0.1 M NaCl, 2 mM $Fe(CN)_6^{3-}$, 35 μg clay. Graph represent results for a single clay film.

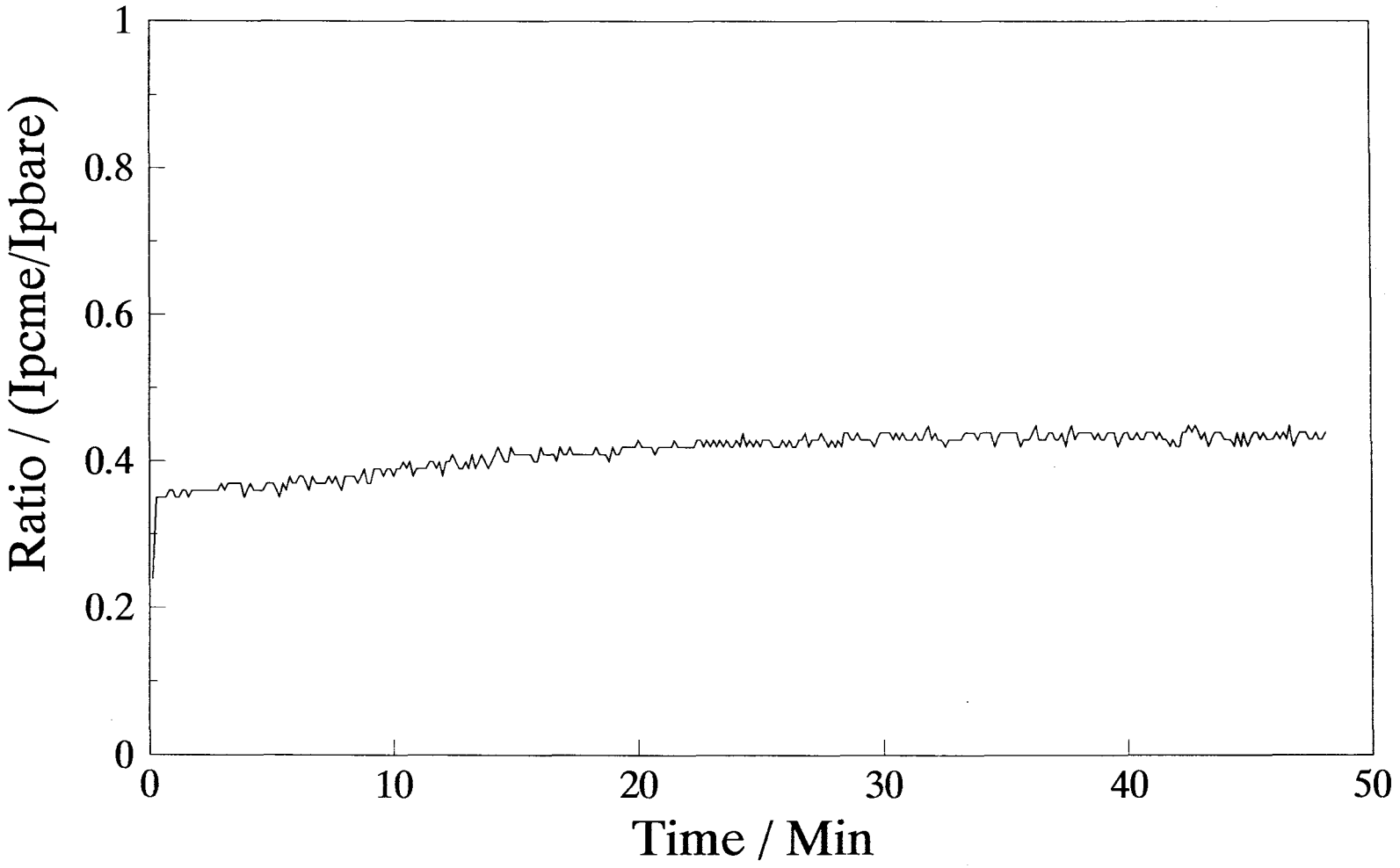
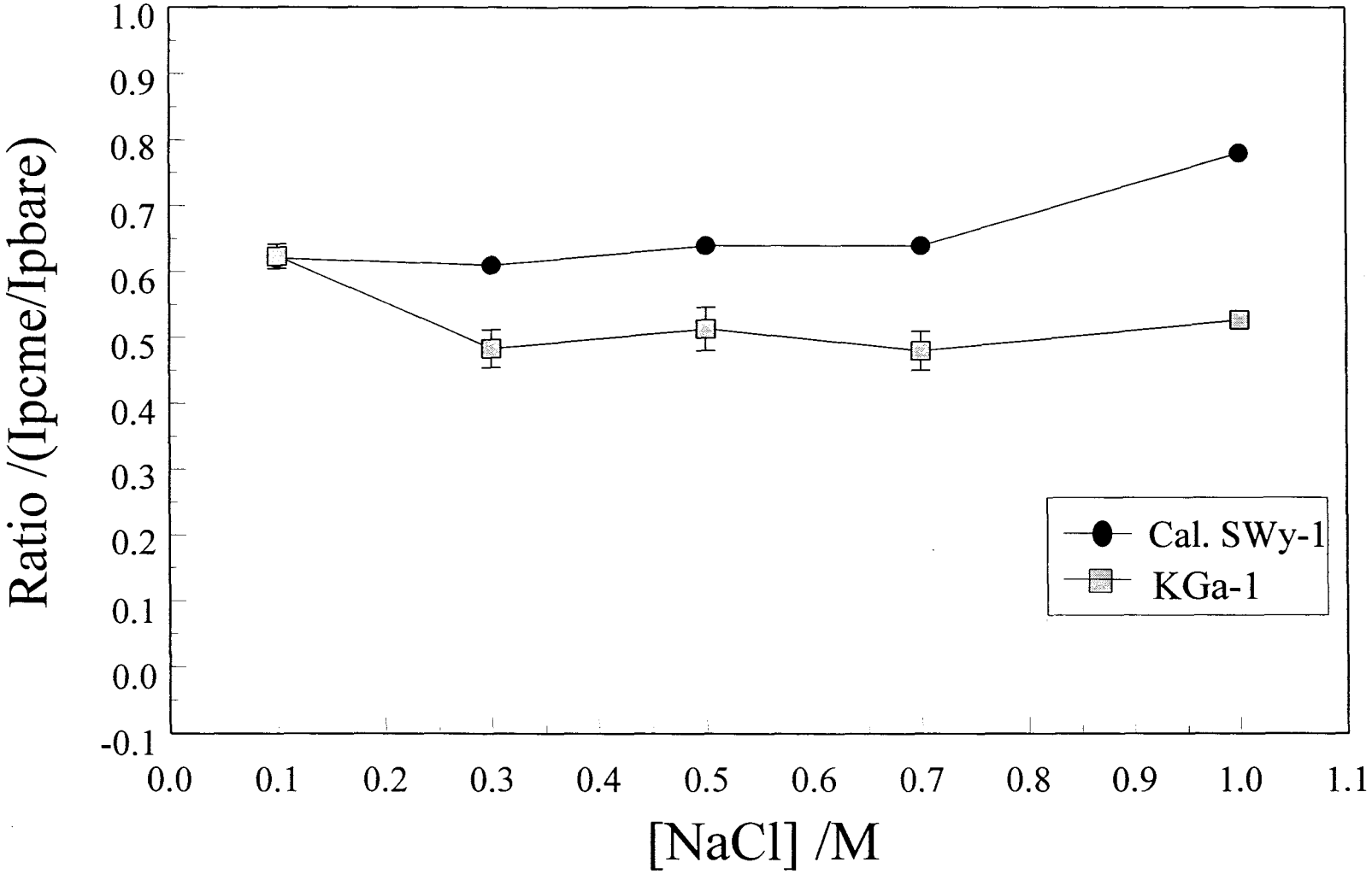

Ratio / (Ipcme/Ipbare)
1
0.8
0.6
0.4
0.2
0
0
10
20
30
40
50
Time / Min

Figure 34: The 45 minute ratioed current for a heat-treated SWy-1 sample as a function of electrolyte concentration. Experimental conditions are 2 mM $Fe(CN)_6^{3-}$, 35 μg clay. Graphs represent an average of three clay films.


Ratio /(Ipcme/Ipbare)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
[NaCl] /M
Cal. SWy-1
KGa-1

The KGa-1 does not swell and has a diffusional response controlled by porous pinholes rather then by the interlayer dimension. The effect of this clay in the mixtures should be quite interesting.

IV.1 Response of Two Component Clay Mixtures to Different Electrolyte Concentrations

Figure 35 shows the results that were obtained for a series of SWy-1/KGa-1 mixtures and compares these results to those for the pure clays. The 50% weight to weight (wt/wt) SWy-1/KGa-1 mixture behaves like SWy-1 while an increasing percentage of KGa-1 results in increasing KGa-1-like behavior. These results indicate that the SWy-1 behavior predominates the diffusion of the $Fe(CN)_6^{3-}$ in a 1:1 mixture but, as the percentage of KGa-1 is increased, the pore-like defects, or pinholes caused by the KGa-1 increasingly become the predominate pathway for diffusion.

In Figure 36, the results that were obtained for a series of SAz-1/KGa-1 mixtures are shown and compared to the results for the pure clays. In this instance, the percentage of SAz-1 had to be increased to 90% wt/wt SAz-1/KGa-1 before there was any evidence of SAz-1 controlled diffusion. In the mixtures with a higher percentage of KGa-1, the ratioed current value is higher then that of the pure KGa-1 film. This indicates that the defects in the films formed from the mixtures are greater then those in the pure KGa-1 clay film.

Figure 35: The 45 minute ratioed current for a series of SWy-1/KGa-1 mixtures as a function of electrolyte concentration. Weight/weight mixture of clays is listed in inset box. Experimental conditions are 2 mM $Fe(CN)_6^{3-}$, 35 μg clay. Graphs represent an average of three clay films.

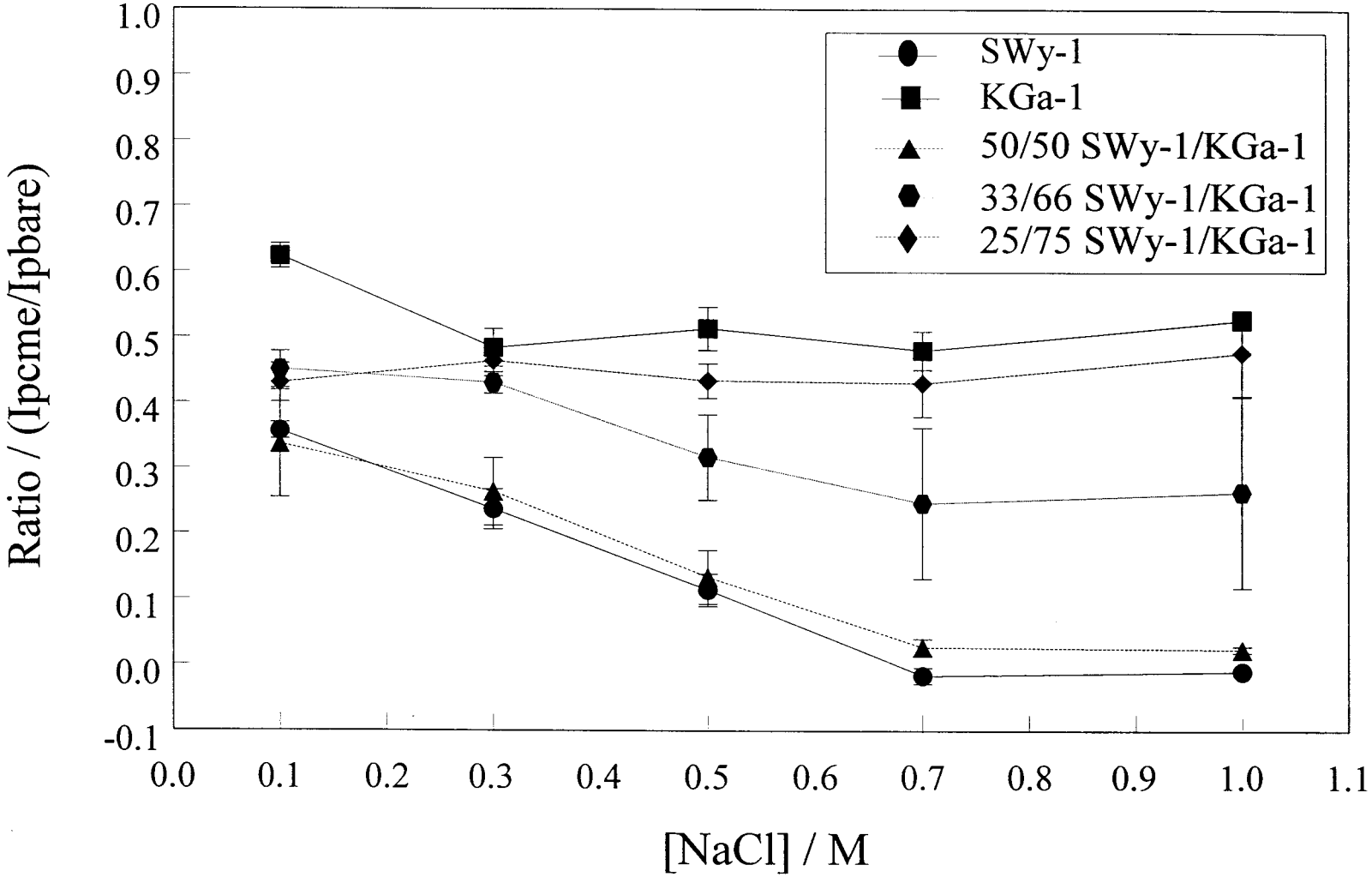
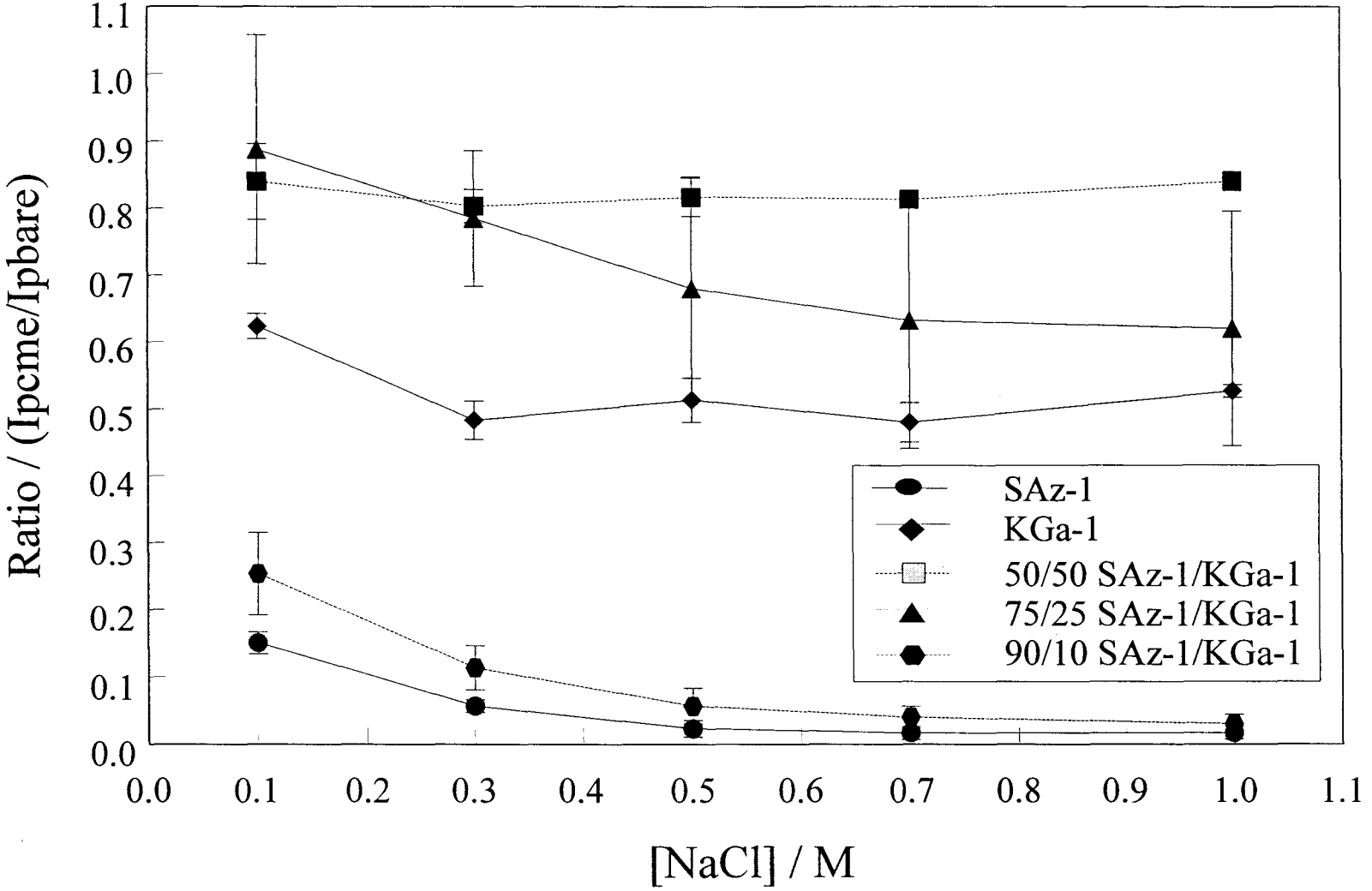

SWy-1
KGa-1
50/50 SWy-1/KGa-1
33/66 SWy-1/KGa-1
25/75 SWy-1/KGa-1
Ratio / (Ipcme/Ipbare)
[NaCl] / M
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1

Figure 36: The 45 minute ratioed current for a series of SAz-1/KGa-1 mixtures as a function of electrolyte concentration. Weight/weight mixture of clays is listed in inset box. Experimental conditions are 2 mM $Fe(CN)_6^{3-}$, 35 μg clay. Graphs represent an average of three clay films.


Ratio / (Ipcme/Ipbare)
[NaCl] / M
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
SAz-1
KGa-1
50/50 SAz-1/KGa-1
75/25 SAz-1/KGa-1
90/10 SAz-1/KGa-1

The results for a 50% wt/wt SWy-1/SAz-1 mixture and those for the pure clays are shown in Figure 37. In this instance, there were no pinholes available for diffusion. The mixture behaves simply like a mixture of the two clays.

IV.2 Three Component Clay Systems

As a continuation of the two component experiments, a series of three component experiments were performed. The response to a series of electrolyte concentrations for a series of mixtures of the three clays is shown in Figure 38. These results indicate that a wt/wt/wt KGa-1 content of 60% produces a mixture where structural defects are a large factor in diffusion. At, or below, a KGa-1 content of 33%, the structural defects have little, if any, effect upon diffusion.

IV.3 Effect of Clay Type on the Diffusional Properties of $Fe(CN)_6^{3-}$ in Mixed Clay Systems

Comparing the results for the different clay mixtures, there are two conclusions. First, the swelling clays do not disrupt one another. Instead, they behave simply like a mixture of the two clays. Secondly, the KGa-1 has a much more disruptive effect in the SAz-1 mixture then in the SWy-1 mixture. Scanning electron microscopy (SEM) was performed on 50/50 wt/wt mixtures of the montmorillonites with the KGa-1. The results support the experimental data in that they show many more disruptions in the KGa-1/SAz-1 film then in the KGa-1/SWy-1 film.

Figure 37: The 45 minute ratioed current for a series of SWy-1/SAz-1 mixtures as a function of electrolyte concentration. Weight/weight mixture of clays is listed in inset box. Experimental conditions are 2 mM $Fe(CN)_6^{3-}$, 35 μg clay. Graphs represent an average of three clay films.

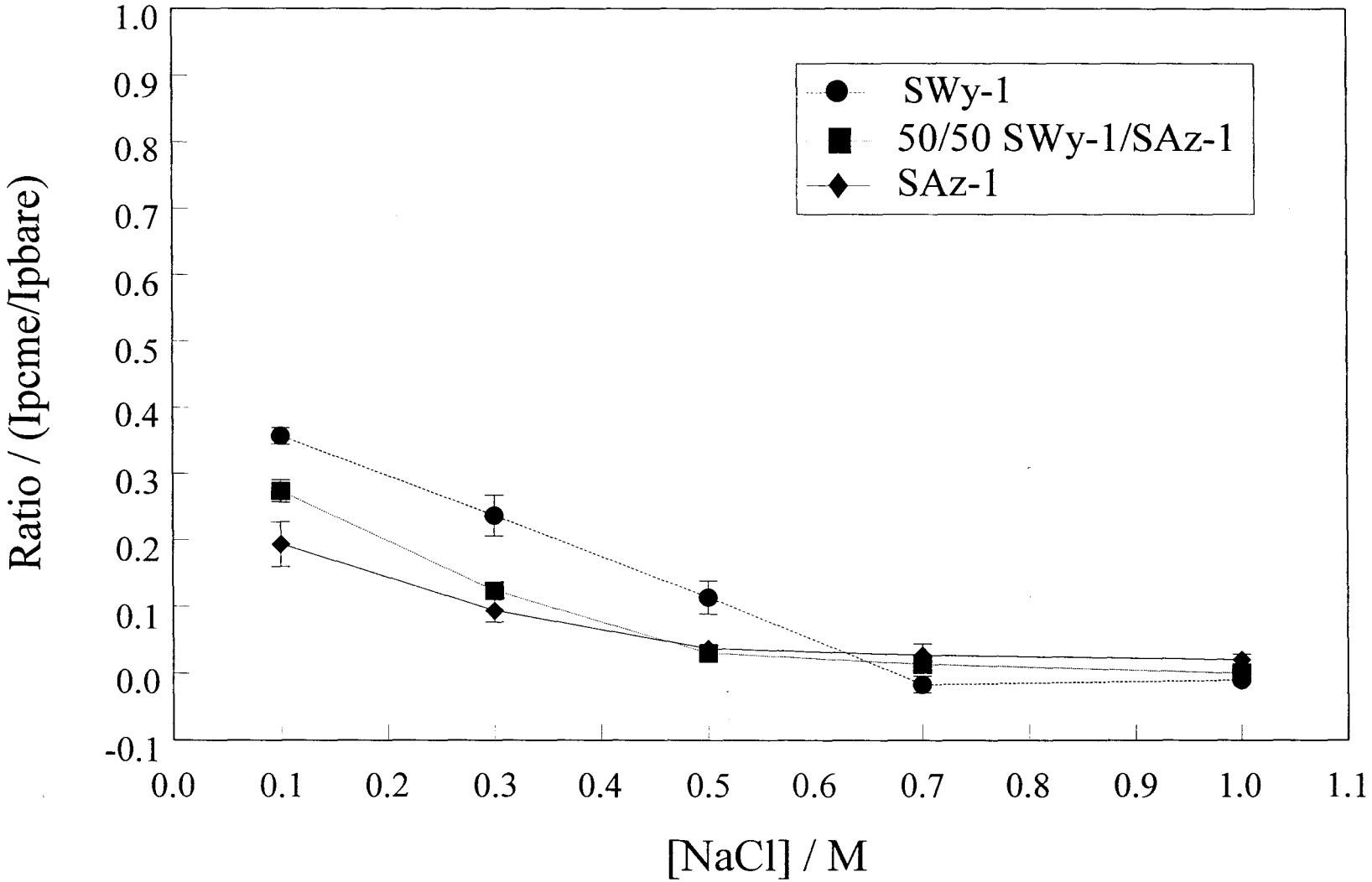
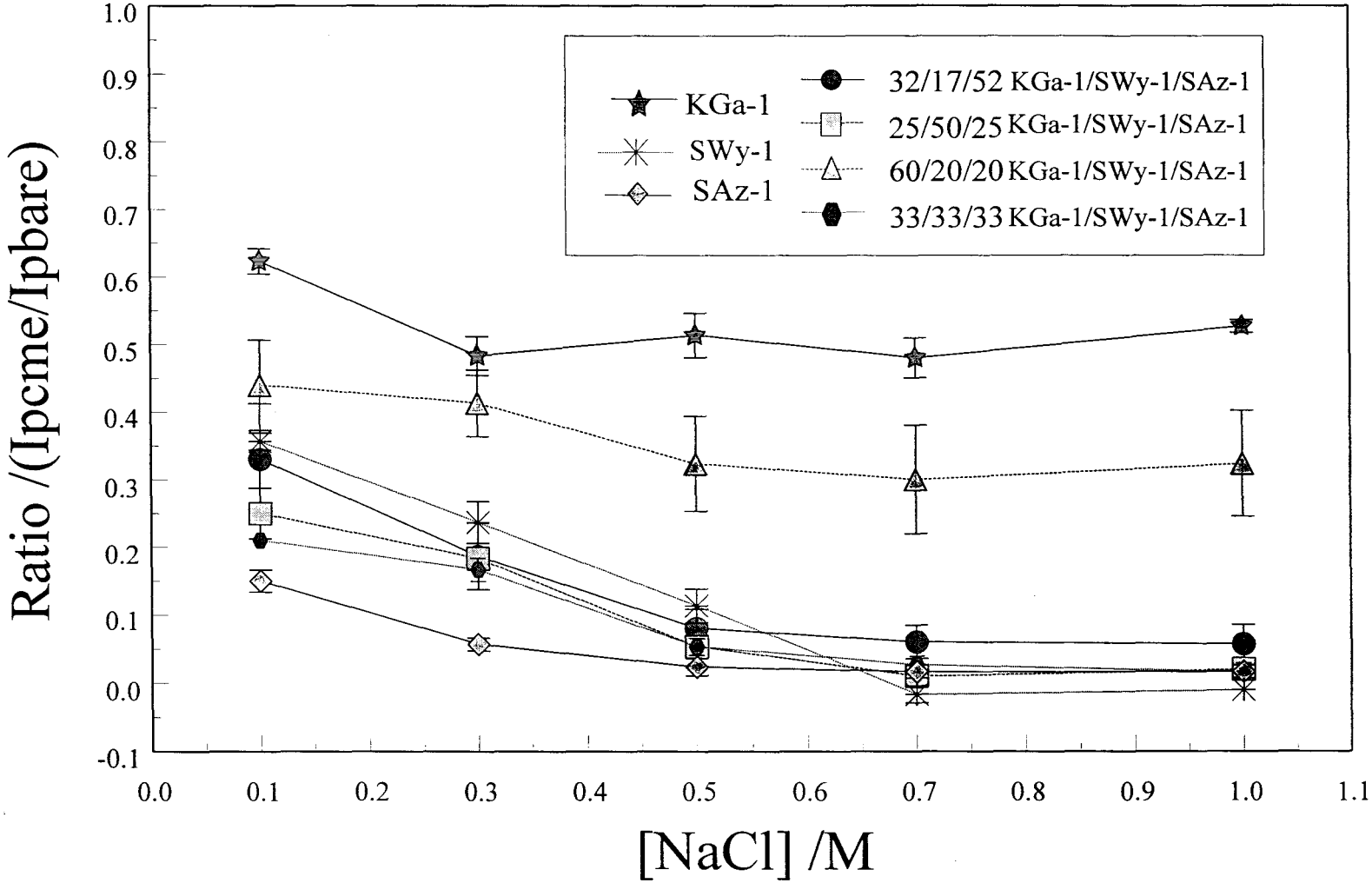

SWy-1
50/50 SWy-1/SAz-1
SAz-1
Ratio / (Ipcme/Ipbare)
[NaCl] / M
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1

Figure 38: The 45 minute ratioed currents for a series of three component clay mixtures as a function of electrolyte concentration. Weight/weight/weight mixture of clays is listed in inset box. Experimental conditions are 2 mM $Fe(CN)_6^{3-}$, 35 μg clay. Graphs represent an average of three clay films.


Ratio /(Ipcme/Ipbare)
[NaCl] /M
KGa-1
SWy-1
SAz-1
32/17/52 KGa-1/SWy-1/SAz-1
25/50/25 KGa-1/SWy-1/SAz-1
60/20/20 KGa-1/SWy-1/SAz-1
33/33/33 KGa-1/SWy-1/SAz-1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1

When the clays are applied to the electrode they are in solution. Therefore, the SWy-1 and the SAz-1 are fully expanded while the KGa-1 is simply suspended in the solution. As the clay droplet is rotated to create the clay film, the expanded clay platelets are able to shift and slide with respect to one another in order to achieve an optimum orientation.[73] It is this shifting that results in well-orientated clay films with the platelets aligned in a parallel manner[11,13]. Because the KGa-1 does not expand its interlayer region, the platelets are not able to reorientate into this optimum configuration. As a result, areas occur in the clay film where the platelets align in a non-parallel manner. It is in these areas that defects occur in the clay film. Because SAz-1 does not swell to the same extent as SWy-1, the SAz-1 platelets are not able to rearrange to as great an extent during the spinning process. As a result, in a mixture of SAz-1 and KGa-1 there will be more defects present in the clay film. In the SWy-1/KGa-1 mixtures, the SWy-1 is able to rearrange around these defects.

In an attempt to mimic the effect of KGa-1 in a clay mixture, the calcined SWy-1 was mixed with a non-treated SWy-1 sample. A 75/25 wt/wt mixture of the calcined SWy-1 to untreated SWy-1 was used. The temporal response of this mixture is shown in Figure 39. From this graph, it is evident that, like the KGa-1, the diffusion of $Fe(CN)_6^{3-}$ through the clay film is immediate. In Figure 40, the response of the mixture to different electrolyte concentrations is shown. This mixture did not have the high ratioed current values seen in the KGa-1/SWy-1 mixture, and it showed a dependence on NaCl concentration. Figure 41 categorizes the results that were seen for the individual clays, for the 75/25 KGa-1/SWy-1 clay mixture and for the 75/25 calcined

Figure 39: Ratioed current as a function of time for a 75:25 wt/wt mixture of heat treated to untreated SWy-1. Experimental conditions are 0.1 M NaCl, 2 mM $Fe(CN)_6^{3-}$, 35 μg clay. Graph represents results for a single clay film.

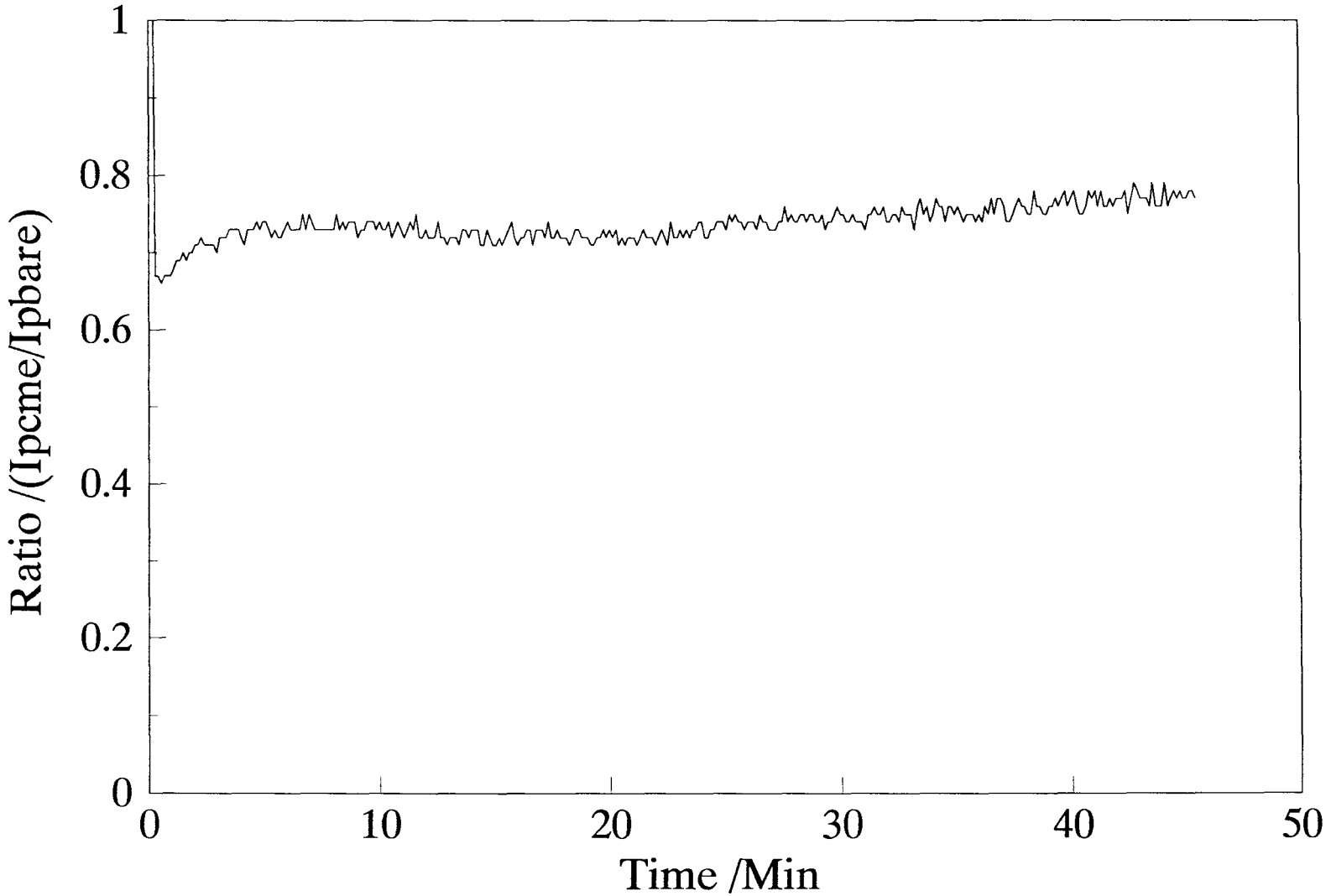

1
0.8
0.6
0.4
0.2
0
Ratio /(Ipcme/Ipbare)
0
10
20
30
40
50
Time /Min

Figure 40: Comparison of the 45 minute ratioed current for a heat-treated SWy-1/SWy-1 sample to a series of SWy-1/KGa-1 mixtures as a function of electrolyte concentration. Weight/weight mixture of clays is listed in inset box. Experimental conditions are 2 mM $Fe(CN)_6^{3-}$, 35 μg clay. Graphs represent an average of three clay films.

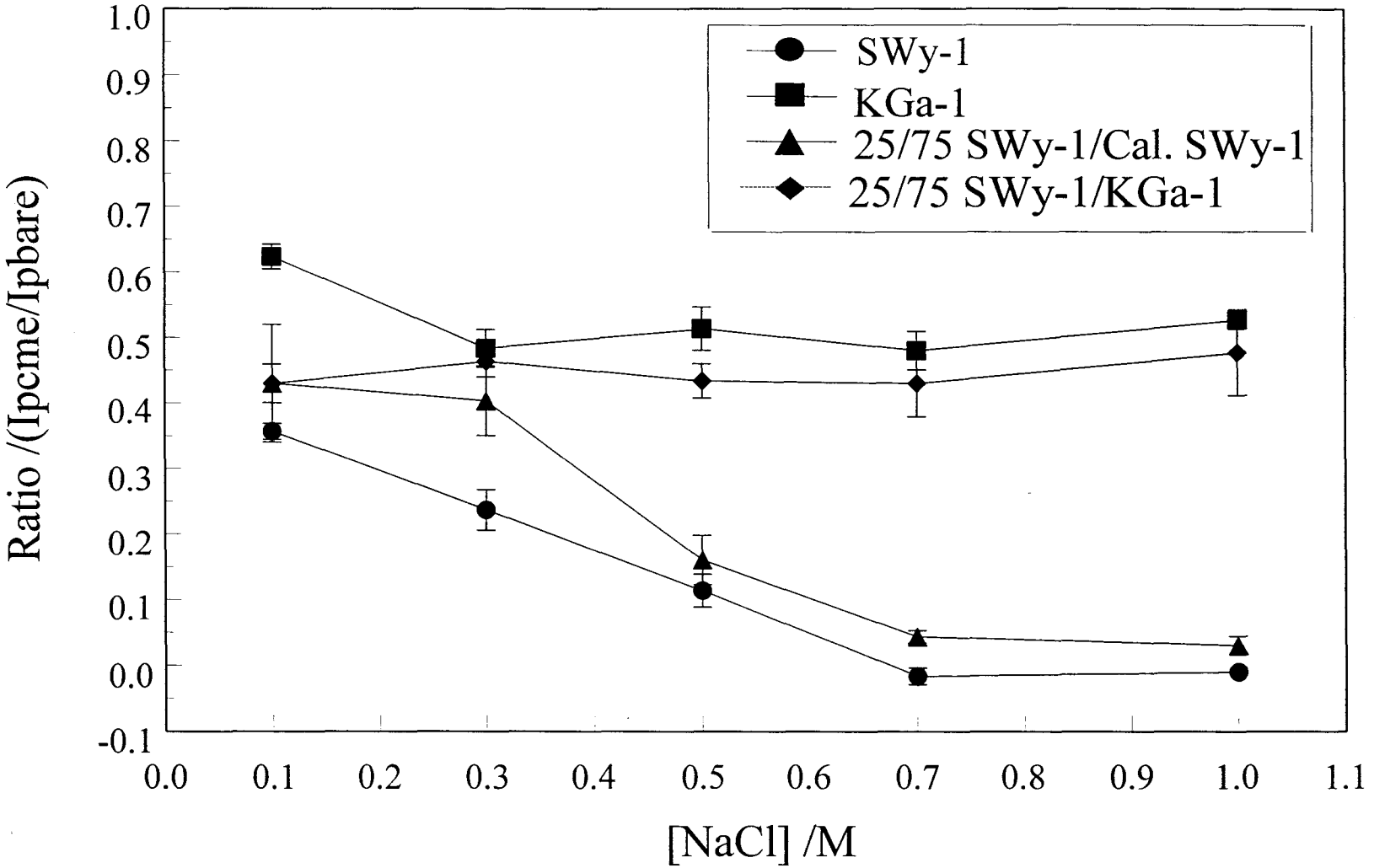

SWy-1
KGa-1
25/75 SWy-1/Cal. SWy-1
25/75 SWy-1/KGa-1
Ratio /(Ipcme/Ipbare)
[NaCl] /M
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1

Figure 41: Categorization of results for single clay and for two mixed clay films. Time dependence is determined from dry into 0.1 M NaCl swelling curves. NaCl dependence is determined from ratioed current as a function of electrolyte concentration experiments.

	Time Dependence	No Time Dependence
[NaCl] Dependence	SWy-1	SAz-1 75/25 Calcined Swy-1/SWy-1
No [NaCl] Dependence		KGa-1 75/25 KGa-1/SWy-1

SWy-1/Swy-1 mixture. The calcined SWy-1/SWy-1 mixture exhibited a response similar to that of the SAz-1 clay-modified electrode. This indicates that like the SAz-1, the response was controlled by the presence of different swelling domains in the clay mixture. While these results were not exactly the same as that of the KGa-1/Swy-1 mixtures, they do confirm that the non-swelling clay is the source of the disruptions in the clay mixture.

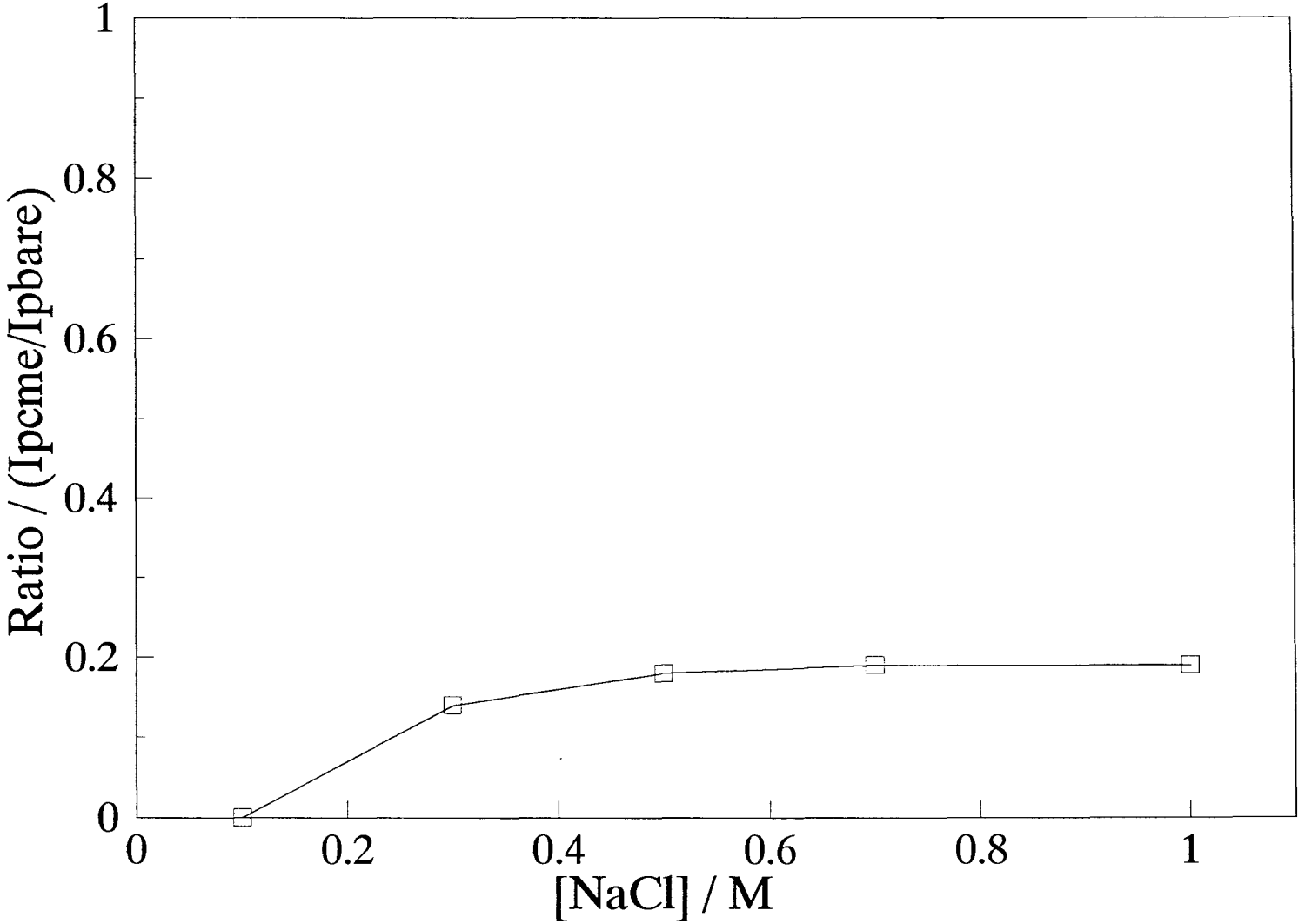
V. Laponite Studies

Laponite is a synthetic trioctahedral hectorite that is manufactured with a very small particle size. It was postulated that the small particle size might lead to differences in the diffusional path of $Fe(CN)_6^{3-}$ through the clay film.

To investigate the swelling of laponite the effect of electrolyte concentration on the ratioed current was determined. These results are presented in Figure 42. As can be seen, the clay film shows no electrolyte dependence until a low electrolyte concentration is reached. At that point the porous clay structure becomes an insulating structure and the ratioed current drops to near zero. These results are attributed to the small particle size of the Laponite. In the Laponite clay film, the particles are so small that the primary path for diffusion is between the clay particles rather than in the interlayer of the clay particles. When the clay swells, the particles expand, and these channels for diffusion become blocked. This results in an insulating clay film.

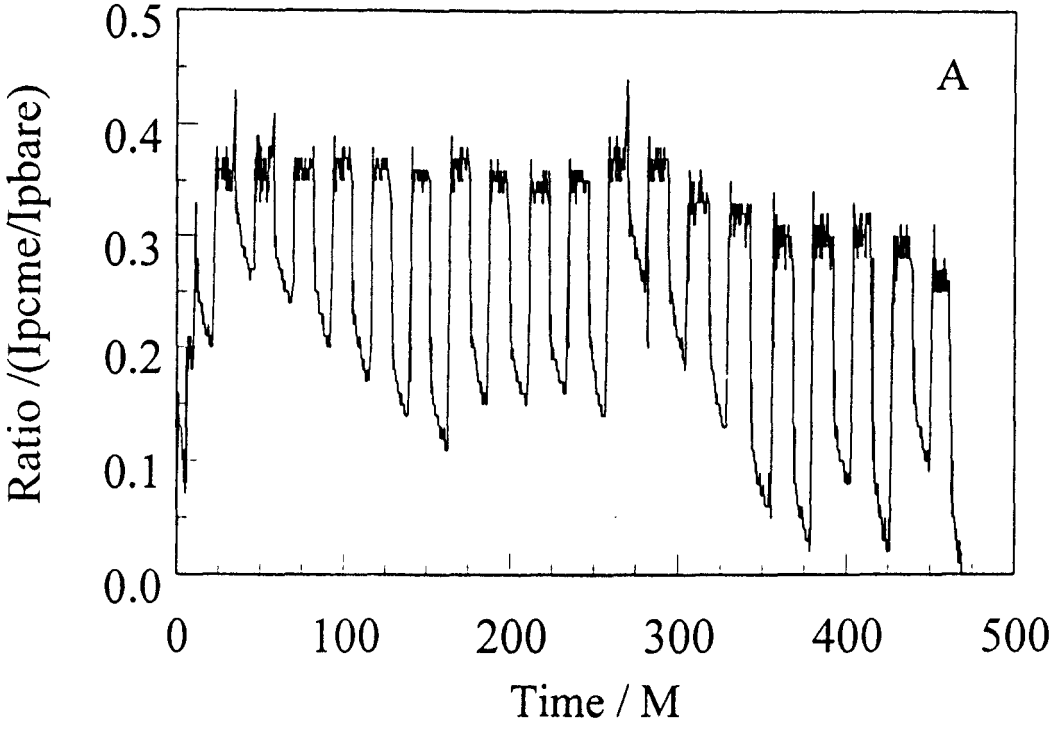
As further verification for this theory, hysterisis within the clay film was examined. If the primary path for diffusion is through defects in the clay film, rather

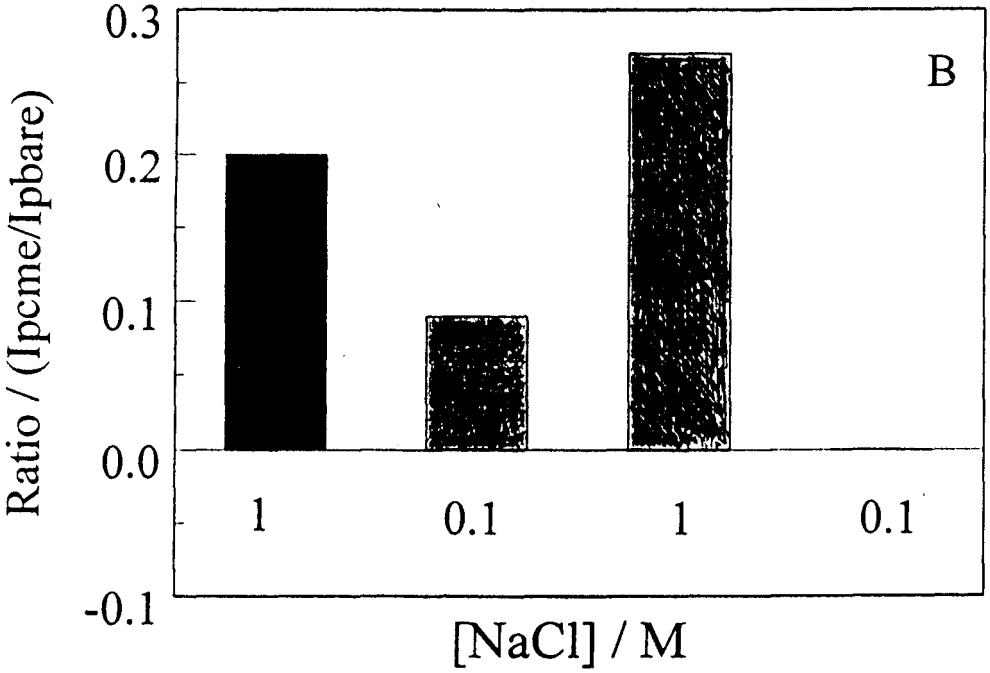
Figure 42: Ratioed current as a function of electrolyte concentration for a Laponite clay film. Experimental conditions are 2 mM $Fe(CN)_6^{3-}$, 35 μg clay. Graph represents averaged results for three clay films.


Ratio / (Ipcme/Ipbare)
1
0.8
0.6
0.4
0.2
0
0
0.2
0.4
0.6
0.8
1
[NaCl] / M

then through the clay interlayer, then the clay film should not be as sensitive to changes in the clay interlayer geometry as are the clays where interlayer diffusion occurs. The results for this study are shown in Figure 43. In the upper portion of this graph, the clay film is switched between 1 M NaCl and 0.1 M NaCl. Due to the long time period for the experiment, a 10 minute equilibration time was used for each electrolyte concentration. The gradual decrease in the current in 0.1 M NaCl is attributed to the short time period for equilibration. Figure 43B shows a series of switches between electrolyte concentrations with a 45 minute equilibration period. In this experiment, reproducible currents were obtained in both electrolyte concentrations. These results indicate that hysterisis does not exist in the clay film. Additionally, they confirm the theory that a small particle size results in diffusion through defects in the film structure rather then through the interlayer region.

Figure 43: A) The effect of electrolyte concentration on the ratioed current at a Laponite clay film. The upper portion of the graph is the current obtained in 1 M NaCl while the lower portion was obtained in 0.1 M NaCl. Electrolyte solutions were switched every 10 minutes. B) The ratioed currents for a Laponite clay film as a function of electrolyte concentration. The clay film was equilibrated in each electrolyte for 45 minutes. Experimental conditions are 2 mM $Fe(CN)_6^{3-}$, 35 μg clay.


A
Ratio /(Ipcme/Ipbare)
0.5
0.4
0.3
0.2
0.1
0.0
0
100
200
300
400
500
Time / M


B
Ratio / (Ipcme/Ipbare)
0.3
0.2
0.1
0.0
-0.1
1
0.1
1
0.1
[NaCl] / M

CHAPTER IV

SUMMARY AND FUTURE DIRECTION

In this project, an automated system to study diffusion through a clay-modified electrode has been developed. This system has been used to study the diffusion of an anion through a clay film. Since both the clay film and the anion are negatively charged the rate of diffusion, or current, for the anion is a direct measure of the ease with which the anion diffuses through the clay film.

The evolution of the current over time and the effect of a number of different conditions on the current have been studied. One of the conditions studied is the affect of clay type on the rate of diffusion. Both the type of clay and the particle size of the clay effect diffusion. The effect of electrolyte concentration on a number of different clay types was studied. In the case of a swelling montmorillonite, electrolyte concentration has a pronounced effect on current. For the non-swelling clay there is no evidence of electrolyte dependence. A very small particle size results in an electrolyte dependence opposite that of the swelling montmorillonites. Temporal studies indicate similiar trends for the different clay types.

Combining the data from the two types of experiments, it is clear that there are two paths for diffusion in the clay film. The first path is through the interlayer region of the clay. This path is electrolyte dependent and is the predominate path in the

swelling montmorillonites. The other path is through fissures in the clay film between non-interacting clay particles. This is the predominate path for diffusion in the non-swelling clays and in the small particle sized clays. In the non-swelling clays this is the only path available for diffusion while in the small particle sized clays, this is the easiest pathway until the clay swells and physically blocks these pathways. Experimental results for mixed clay systems indicate that in mixture of the swelling and non-swelling clays both paths exist. The predominance of one path over the other is a result of the percentages present in the mixtures and the degree that the swelling montmorillonite is able to swell.

The new system has also been used to study factors that affect the interlayer spacing in a swelling montmorillonite. The temporal response of the clay film to changing conditions was followed. It was found that a dry clay film and a clay film that had been previously equilibrated in a strong electrolyte concentration had the same response to a low electrolyte concentration. In other words, previous exposure to a concentrated electrolyte did not affect the clay film's response. In contrast, a previously swollen clay film exhibited hysterisis in sodium chloride solutions. In a potassium chloride solution, however, the clay film eventually collapsed. Temperature affected the temporal nature of this response but it did not affect the final interlayer spacing. These results are contrary to the predicted results from double layer theory and, consequently, support the hydration theory for clay swelling. In summary, the phenomenon of clay swelling, which, before has been studied only in its final equilibrium state, is now open to kinetic analysis.

The new system has opened up many new areas of research. These areas include the effect of particle size and swelling ability on the diffusional properties of the clay, the effect of temperature on the swelling of the clay, and the phenomena of hysterisis in the clay. While the above study touched on all these aspects, none of these areas were studied to exhaustion. Additionally, the diffusion of cations or organics through the clay film can be studied with the new system. These studies are limited only by the requirement that the species of interest be electroactive. In conclusion, the new system has opened up many exciting areas of study to intimate examination through the use of clay-modified electrodes.

APPENDIX 1

COMPUTER PROGRAMS DEVELOPED

FOR

AUTOMATED ELECTROCHEMICAL SYSTEM

```
10 ' 2wetemp.bas
20 ' April 15, 1994
30 ' Program to collect only every Xth scan
40 ' uses mode 5 to get the data and mode 9 to retrieve it
50 ' incorporates thermocouple to monitor temperature
60 '
70 ' STRATEGY: Open file #3.  Use Mode 5a to collect the first bit of data.
80 '    retrieve the data from the computer using mode 9a.
        While getting the next
90 '    bit of data (Mode 5b) write the first bit of data to file #3.  Use mode 8
100 'to check the status of Mode 5b while doing this to ensure that time is
110 'resolved - if not the program stops.  Repeat this process until the user
120 'stops it.  Data is then sorted and the user is given options on further
130 'manipultations which are to be performed
140 'Uses A Timer to wait a specific  period to collect all scans
150 'Uses Mode 19 to wait for the start of a scan to begin data collection
160 '
170 CLEAR
180 '
190 '****These are counters used for retaining the Ipc, etc
200 '
210     NCHAN%=3:SR2=5000:G=3:G2=0:SRATE4=500:NUMBSCANS=0:
        SCALE=1:SCALE1=1
220 CATMIN=0:ANMAX=.4:XTH=5:START=20
230 DIM JS(9)
240 CLS
250 '
260 '****This is the user input area - can use defaults or change info
270 '
280 PRINT:PRINT"THIS IS THE PROGRAM FOR TWO WORKING ELECTRODES"
290 PRINT"Uses the stepper motor to position the electrodes"
300 PRINT"Presumes that the CME is run through the amp and that"
310 PRINT"the bare electrode is run through the I-E converter"
320 PRINT:PRINT"Your default settings are as follows:"
330 PRINT:PRINT"Starting Voltage = +0.8V
340 PRINT"Switching Voltage = -0.2V"
350 PRINT"Scan rate = 500 mV/s"
360 PRINT"Scaling for CME (run through the Amp) = 10x10^-6 A/V"
370 PRINT"Scaling for the Bare Electrode (run through the I-E) =
        9.96x10^-6 A/V"
380 PRINT"Sampling rate = 500 Hz"
390 PRINT"Full Scale Voltage Range for the X axis = 2.5 V"
400 PRINT"Full Scale Voltage Range for the Y axis = 20 V"
410 PRINT"Voltage maxima for the peak cathodic current = 0 V"
```

```
420 PRINT"Voltage minima for the peak anodic current = 0.4 V"
430 PRINT"Number of Scans Collected = Every 5th"
440 PRINT"Number of first scans collected = 20"
450 PRINT:PRINT"Do you want to change any of these settings? If so enter
      <y>"
460 A$=INKEY$:IF A$="" THEN GOTO 460 ELSE GOTO 470
470 IF A$="Y" OR A$="y" THEN GOTO 480 ELSE GOTO 1240
480 PRINT"Do you have the parameters you wish to use saved in a file?"
490 PRINT"Hit <y> if you do, otherwise hit anykey to continue"
500 A$=INKEY$:IF A$="" THEN GOTO 500 ELSE GOTO 510
510 IF A$="Y" OR A$="y" THEN GOTO 520 ELSE GOTO 720
520 INPUT"Input the name of the file in which the parameters are
      saved:";EXPS$
530 OPEN "c:\mccme\expara\"+EXPS$ FOR INPUT AS #1
540 INPUT #1, VS
550 INPUT #1, VSW
560 INPUT #1, SCAN
570 INPUT #1, AMP2#
580 INPUT #1, QCONV2
590 INPUT #1, AMP#
600 INPUT #1, QCONV
610 INPUT #1, SRATE4
620 INPUT #1, G
630 INPUT #1, G2
640 INPUT #1, N
650 INPUT #1, NPTS%
660 INPUT #1, CATMIN
670 INPUT #1, ANMAX
680 INPUT #1, XTH
690 INPUT #1, START
700 CLOSE #1
710 GOTO 1250
720 INPUT"Input your starting voltage (in Volts)";VS
730 INPUT"Input your switching voltage (in Volts)";VSW
740 INPUT"Input the scan rate you will be using (in mV/sec):";SCAN
750 XRNG=(ABS(VS))+(ABS(VSW))
760 XSTP=(XRNG/10)
770 N2=INT((2*XRNG)*(1/(SCAN/1000)))
780 INPUT"Input the amplification for the CME (amp) (in amps/volt):";AMP2#
790 QCONV2=(AMP2#/.000001)
800 INPUT"Input the amplification for the Bare Electrode (I-E)
      (in amps/volt):";AMP#
810 QCONV=(AMP#/.000001)
820 PRINT:PRINT"A single scan will take x seconds. x=";N2
```

```
830 PRINT"If you skip this step your sampling rate will be 500 Hz"
840 PRINT"Do you want to change the sampling rate? If so hit <y>"
850 A$=INKEY$:IF A$="" THEN GOTO 850 ELSE GOTO 860
860 IF A$="Y" OR A$="y" THEN GOTO 870 ELSE GOTO 960
870 INPUT"Input your desired sampling rate";SRATE
880 SRATE2=INT(10000000#/SRATE)
890 SR2=INT(SRATE2/4)
900 SRATE3=(4*SR2)
910 SRATE4=(10000000#/SRATE3)
920 PRINT"Actual sampling rate is:";SRATE4
930 PRINT"If this is acceptable hit <Y>"
940 A$=INKEY$:IF A$="" THEN GOTO 940 ELSE GOTO 950
950 IF A$="Y" OR A$="y" GOTO 960 ELSE GOTO 870
960 NTEMP=INT(N2*SRATE4)
970 NTEMP2=INT(NTEMP/3)
980 N=NTEMP2*3
990 IF N>10000 THEN GOTO 1000 ELSE GOTO 1010
1000 PRINT"Your Number of Points/Scan is too high.  You need to choose a
       slower rate":GOTO 870
1010 NPTS%=N/NCHAN%
1020 PRINT:PRINT"The default scaling for the X axis is 2.5 V full scale"
1030 PRINT:PRINT"The default scaling for the Y axis is 20 V full scale"
1040 PRINT"Do you want to change the scaling? If so hit <y>"
1050 A$=INKEY$:IF A$="" THEN GOTO 1050 ELSE GOTO 1060
1060 IF A$="Y" OR A$="y" THEN GOTO 1070 ELSE GOTO 1150
1070 PRINT"You can change the scaling for the voltage and current as
       follows:"
1080 PRINT"To get a Full Scale Voltage of:  CHOOSE:"
1090 PRINT"                          20V     0"
1100 PRINT"                          10V     1"
1110 PRINT"                           5V     2"
1120 PRINT"                         2.5V     3"
1130 PRINT:INPUT"Enter the desired scaling(choose 0-3)
       for the Potential:";G
1140 INPUT"Enter the desired scaling (choose 0-3) for the working
       electrodes:";G2
1150 INPUT"Enter the minimum voltage at which the peak cathodic current
       will be seen";CATMIN
1160 INPUT"Enter the maximum voltage at which the peak anodic current will
       be seen";ANMAX
1170 INPUT"Enter the number of every Xth scan which you wish to
       collect";XTH
1180 PRINT"The default is to collect the first 10 scans"
1190 PRINT"Do you want to change this to the first X scans?"
```

```
1200 A$=INKEY$: IF A$="" THEN GOTO 1200 ELSE GOTO 1210
1210 IF A$="Y" OR A$="y" THEN GOTO 1220 ELSE GOTO 1230
1220 INPUT"Input the number of beginning scans for which you wish to
       collect them all";START
1230 IF NUMBSCANS=1 GOTO 1330 ELSE GOTO 1250
1240   VS=.8:VSW=-.2:SCAN=500:AMP2#=.00001:QCONV2=10:
       AMP#=.0000996:QCONV=9.96:N2=4
1250 XRNG=(ABS(VS))+(ABS(VSW))
1260 XSTP=(XRNG/10)
1270 N2=INT((2*XRNG)*(1/(SCAN/1000)))
1280 N=N2*SRATE4
1290 NTEMP=INT(N/3)
1300 NRND=NTEMP*3
1310 NPTS%=N/NCHAN%
1320 DIM DDA%(N),DDB%(N),R%(NPTS%,2)
1330 QMAX=0:QMIN=0:QMAX2=0:QMIN2=0:QMXBR=0:QMNBR=0
1340 EQMN=0:EQMX=0:EQMN2=0:EQMX2=0:RMAX=0
1350 XTHTIME=(XTH*N2)
1360 CNTR=1:CNTR2=0
1370 PRINT:PRINT"Remember to Choose a different file name from before!"
1380 INPUT "Input the name of the file to which the raw data will be
       saved:";B$
1390 INPUT"Input the name of the file to which the data for time of collection
       will be saved:";C$
1400 PRINT"Hit <G> to continue";
1410 A$=INKEY$: IF A$="" GOTO 1410
1420 IF A$="G" OR A$="g" THEN GOTO 1460 ELSE GOTO 1400
1430 '
1440 '***Writes the number of the scans which are first collected to time file
1450 '
1460 OPEN "c:\mccme\data\"+C$ FOR APPEND AS #1
1470 WRITE #1, START
1480 CLOSE #1
1490 '
1500 '***Sets up the screen output during data acquisition
1510 '
1520 CLS:KEY OFF
1530 LOCATE 3,60
1540 PRINT "Hit <Q> to Quit"
1550 LOCATE 3,10
1560 PRINT"Acquiring Data"
1570 LOCATE 5,10
1580 PRINT"Time at Start:"
1590 LOCATE 7,10
```

```
1600 PRINT"Temperature inside Cell:"
1610 LOCATE 9,10
1620 PRINT"Number of Scans Acquired:"
1630 '
1640 ' ***Sets up the conversions for data and graphing
1650 '
1660 IF G=0 THEN CONV=(20/65536!)
1670 IF G=1 THEN CONV=(10/65536!)
1680 IF G=2 THEN CONV=(5/65536!)
1690 IF G=3 THEN CONV=(2.5/65536!)
1700 IF G2=0 THEN CONV2=(20/65536!)
1710 IF G2=1 THEN CONV2=(10/65536!)
1720 IF G2=2 THEN CONV2=(5/65536!)
1730 IF G2=3 THEN CONV2=(2.5/65536!)
1740 X1=INT(-VS/(CONV))
1750 XTRA=INT(.01/CONV)
1760 STCOLL=ABS(X1)-ABS(XTRA)
1770 X2=INT(-VSW/(CONV))
1780 Y1=8
1790 Y2=632
1800 XMEAN=(X2+X1)/2
1810 YMEAN=(Y2+Y1)/2
1820 A2=((X1-XMEAN)^2)+((X2-XMEAN)^2)
1830 B2=((Y1-YMEAN)^2)+((Y2-YMEAN)^2)
1840 AB=((X2-XMEAN)*(Y2-YMEAN))+((X1-XMEAN)*(Y1-YMEAN))
1850 SLOPE=AB/A2
1860 YINT=YMEAN-(SLOPE*XMEAN)
1870 '
1880 '****INITIALIZATION OF MSTEP****
1890 '
1900 DEF SEG=&H7000
1910 BLOAD "C:\MCCME\MSTEP\MSTEP.BIN",0
1920 MSTEP=0
1930 MD%=12
1940 STP#=0
1950 FLAG%=0
1960 D%(0)=0
1970 D%(1)=255
1980 D%(2)=80
1990 D%(3)=1000
2000 D%(4)=2
2010 D%(5)=0
2020 D%(6)=0
2030 D%(7)=0
```

```
2040 D%(8)=1
2050 D%(9)=&H330
2060 CALL MSTEP (MD%, D%(0), STP#, FLAG%)
2070 IF FLAG%<>0 THEN PRINT "Error in initializing #";FLAG%:STOP
2080 '
2090 ' SUBROUTINE TO MOVE THE MOTOR X STEPS
2100 '
2110 MD%=4
2120 D%(0)=0
2130 D%(1)=20
2140 STP#=2000
2150 CALL MSTEP (MD%, D%(0), STP#, FLAG%)
2160 MD%=8
2170 CALL MSTEP(MD%,D%(0),STP#,FLAG%)
2180 IF FLAG%=0 THEN GOTO 2220 ELSE GOTO 2160
2190 '
2200 '***** INITIALIZATION OF DAC
2210 '
2220 GOSUB 10000
2230 '
2240 ' **** INITIAL TEMPERATURE
2250 '
2260 GOSUB 20000
2270 '
2280 '***SETS UP THE DAC TO SEND OUT ONE LOW PULSE***
2290 GOSUB 10250
2300 '
2310 D%(0)=1
2320 MD%=10
2330 CALL HRES(MD%,D%(0),FLAG%)
2340 IF FLAG%<>0 THEN PRINT"error in setting counter configuration.
       Error #";FLAG%:STOP
2350 OUT BASE%+10,2
2360 'LINE 850 TURNS ON BIT 2 OF COUNTER ENABLE SYSTEM
2370 '
2380 '******* DATA COLLECTION SUBROUTINES
2390 '
2400 '
2410 ' Data collection for all points at beginning
2420 '
2430 IF CNTR<= START THEN GOSUB 30010
2440 ' Data collection for every Xth pt rather then all pts
2450 CLOSE #3
2460 CNTR=START+XTH
```

```
2470 GOSUB 20000
2480 '
2490 ' Data collection for every Xth pt rather then all pts
2500 '
2510 ON TIMER(XTHTIME) GOSUB 2590
2520 TIMER ON
2530 GOTO 2530
2540 '
2550 '***Tells it to wait until a certain voltage is reached to start collecting
2560 '
2570 ' Routine to collect Data
2580 '
2590 GOSUB 10250
2600 GOSUB 40010
2610 '
2620 ' Collect Temperature as well
2630 '
2640 GOSUB 20000
2650 '
2660 RETURN
2670 '
2680 '**** Option to graph the data
2690 '
2700 CLOSE #3
2710 OPEN "c:\mccme\data\exps" FOR APPEND AS #1
2720 WRITE #1, B$
2730 WRITE #1, CNTR
2740 CLOSE #1
2750 CLS: LOCATE 5,5:PRINT"Do you want to graph the data?"
2760 A$=INKEY$:IF A$="" GOTO 2760
2770 IF A$="y" OR A$="Y" GOTO 2780 ELSE GOTO 3500
2780 INPUT"Input the conditions you used (no commas)";COND$
2790 CLS:SCREEN 2:KEY OFF
2800 LOCATE 20,2
2810 PRINT VS
2820 I=1
2830 FOR J=(VS-XSTP) TO VSW STEP -XSTP
2840 LOCATE 20, 74/10*(I)
2850 PRINT USING"#.#";J
2860 I=I+1
2870 NEXT J
2880 LOCATE 20,74
2890 PRINT VSW
2900 FOR I=3 TO N-2 STEP 3
```

```
2910 J=I+1
2920 K=J+1
2930 X=(YINT+(DDA%(I)*SLOPE)*-1)
2940 Y1=(100-((DDA%(J)*CONV2*10)*QCONV2*SCALE))
2950 LINE -(X,Y1)
2960 NEXT I
2970 FOR I=3 TO N-2 STEP 3
2980 J=I+1
2990 K=J+1
3000 X=(YINT+(DDA%(I)*SLOPE)*-1)
3010 Y2=(100-((DDA%(K)*CONV2*10)*QCONV*SCALE1))
3020 LINE -(X,Y2)
3030 NEXT I
3040 LOCATE 2,1
3050 PRINT"Do you need to change the scaling factor?"
3060 A$=INKEY$:IF A$="" THEN GOTO 3060 ELSE GOTO 3070
3070 IF A$="Y" OR A$="y" THEN GOTO 3080 ELSE GOTO 3130
3080 PRINT"The scaling factor for the CME is";SCALE
3090 INPUT"Input the new scaling factor for the CME";SCALE
3100 PRINT"The scaling factor for the bare electrode is";SCALE1
3110 INPUT"Input the new scaling factor for the bare electrode";SCALE1
3120 GOTO 2800
3130 CLS
3140 LOCATE 5,1
3150 PRINT COND$
3160 LOCATE 20,2
3170 PRINT VS
3180 I=1
3190 FOR J=(VS-XSTP) TO VSW STEP -XSTP
3200 LOCATE 20, 74/10*(I)
3210 PRINT USING"#.#";J
3220 I=I+1
3230 NEXT J
3240 LOCATE 20,74
3250 '
3260 PRINT VSW
3270 FOR I=3 TO N-2 STEP 3
3280 J=I+1
3290 K=J+1
3300 X=(YINT+(DDA%(I)*SLOPE)*-1)
3310 Y1=(100-((DDA%(J)*CONV2*10)*QCONV2*SCALE))
3320 LINE -(X,Y1)
3330 NEXT I
3340 FOR I=3 TO N-2 STEP 3
```

```
3350 J=I+1
3360 K=J+1
3370 X=(YINT+(DDA%(I)*SLOPE)*-1)
3380 Y2=(100-((DDA%(K)*CONV2*10)*QCONV*SCALE1))
3390 LINE -(X,Y2)
3400 NEXT I
3410 LOCATE 2,1
3420 PRINT"Hit <printscreen> to print"
3430 LOCATE 3,1
3440 PRINT"type <exit> when done"
3450 LOCATE 21,5
3460 SHELL
3470 '
3480 ' OPTIONS TO CONTINUE EXPERIMENTS
3490 '
3500 CLS
3510 PRINT:PRINT"Choose an option"
3520 PRINT"1. Move the electrodes out of solution"
3530 PRINT"2. Do another experiment - Change the experimental
       parameters"
3540 PRINT"3. Do another experiment - Keep the same parameters"
3550 PRINT"4. Print out the experimental parameters used in the experiment"
3560 PRINT"5. Save the experimental parameters used in the experiment"
3570 PRINT"6. Quit"
3580 A$=INKEY$: IF A$="" GOTO 3580
3590 A=VAL(A$)
3600 ON A GOTO 3660,3610,1330,3790,4080,4330
3610 NUMBSCANS=1
3620 GOTO 480
3630 '
3640 'MOVE MSTEP BACK
3650 '
3660 DEF SEG=&H7000
3670 MD%=4
3680 D%(0)=0
3690 D%(1)=20
3700 STP#=-2000
3710 CALL MSTEP (MD%, D%(0), STP#, FLAG%)
3720 MD%=8
3730 CALL MSTEP(MD%,D%(0),STP#,FLAG%)
3740 IF FLAG%=0 THEN GOTO 3750 ELSE GOTO 3720
3750 GOTO 3500
3760 '
3770 '****Routine to Print out Experimental Parameters
```

```
3780 '
3790 CLS
3800 PRINT:PRINT"Starting Voltage =";VS
3810 PRINT"Switching Voltage =";VSW
3820 PRINT"Scan rate =";SCAN
3830 PRINT"Scaling for the CME (amp) =";AMP#
3840 PRINT"Scaling for the bare electrode (I-E)=";AMP2#
3850 PRINT"Sampling rate =";SR2
3860 IF G=0 THEN FSV=20
3870 IF G=1 THEN FSV=10
3880 IF G=2 THEN FSV=5
3890 IF G=3 THEN FSV=2.5
3900 IF G2=0 THEN FSV2=20
3910 IF G2=1 THEN FSV2=10
3920 IF G2=2 THEN FSV2=5
3930 IF G2=3 THEN FSV2=2.5
3940 PRINT"Full Scale Voltage Range for the Applied Potential =";FSV;"V"
3950 PRINT"Full Scale Voltage Range for the Current =";FSV2;"V"
3960 PRINT"Name of file that raw data was stored to is:  ";B$
3970 LPRINT"Starting Voltage =";VS
3980 LPRINT"Switching Voltage =";VSW
3990 LPRINT"Scan rate =";SCAN
4000 LPRINT"Scaling for the CME (amp) =";AMP#
4010 LPRINT"Scaling for the Bare Electrode (I-E)=";AMP2#
4020 LPRINT"Sampling rate =";SR2
4030 LPRINT"Full Scale Voltage Range for the Applied Potential =";FSV;"V"
4040 LPRINT"Full Scale Voltage Range for the Current =";FSV2;"V"
4050 LPRINT"Name of file that data was stored to is:  ";B$
4060 PRINT:PRINT:PRINT"Hit anykey to continue"
4070 Z$=INKEY$:IF Z$="" THEN 4070 ELSE GOTO 3500
4080 '
4090 ' Routine to Save parameters Used
4100 '
4110 CLS
4120 INPUT"Input the name of file to which the information will be saved";XP$
4130 OPEN "c:\mccme\expara\"+XP$ FOR OUTPUT AS #1
4140 WRITE #1, VS
4150 WRITE #1, VSW
4160 WRITE #1, SCAN
4170 WRITE #1, AMP2#
4180 WRITE #1, QCONV2
4190 WRITE #1, AMP#
4200 WRITE #1, QCONV
4210 WRITE #1, SRATE4
```

```
4220 WRITE #1, G
4230 WRITE #1, G2
4240 WRITE #1, N
4250 WRITE #1, NPTS%
4260 WRITE #1, CATMIN
4270 WRITE #1, ANMAX
4280 WRITE #1, XTH
4290 WRITE #1, START
4300 CLOSE #1
4310 GOTO 3500
4320 '
4330 CLS:PRINT"NOTE!"
4340 PRINT:PRINT"In order to assure your files are saved"
4350 PRINT"you need to transfer them to a floppy disc"
4360 PRINT:PRINT"Do you want to do this now?"
4370 PRINT"NOTE! It is MUCH faster to do this once you are out of this
       program!"
4380 PRINT"c:\mccme\data\files contains the names of the files to which the
       data was saved"
4390 PRINT:PRINT"Hit <y> if you want to transfer your files now"
4400 A$=INKEY$:IF A$="" GOTO 4400
4410 IF A$="y" OR A$="Y" GOTO 4420 ELSE GOTO 4610
4420 PRINT"Names of files which contain the scans:"
4430 PRINT"Number of scans in file:"
4440 OPEN "c:\mccme\data\exps" FOR INPUT AS #1
4450 IF EOF(1) GOTO 4490 ELSE GOTO 4460
4460 LINE INPUT #1, L$
4470 PRINT L$
4480 GOTO 4450
4490 CLOSE #1
4500 INPUT"Enter name of file to save:";I$
4510 INPUT"Enter name of file to copy it to (specify drive):";D$
4520 OPEN "C:\mccme\data\"+I$ FOR INPUT AS #1
4530 OPEN D$ FOR OUTPUT AS #2
4540 IF EOF(1) GOTO 4580
4550 LINE INPUT #1, L$
4560 WRITE #2, L$
4570 GOTO 4540
4580 CLOSE #1
4590 CLOSE #2
4600 GOTO 4390
4610 CLS
4620 PRINT:PRINT"TYPE SYSTEM to RETURN to DOS"
4630 END
```

```
10000 '
10010 '***PROGRAM TO INITIALIZE THE DAC
10020 '
10030 '***program to initialize the dac
10040 '
10050 LOCATE 3,30:PRINT TIME$
10060 FOR I=1 TO 9
10070 D%(I)=0
10080 NEXT I
10090 DEF SEG = &H6000
10100 BLOAD "c:\mccme\dac\hres.bin",0
10110 OPEN "c:\MCCME\DAC\HRES.CFG" FOR INPUT AS #1
10120 INPUT #1,BASE%
10130 CLOSE #1
10140 D%(0)=BASE%
10150 D%(1)=7
10160 D%(2)=1
10170 D%(3)=0
10180 HRES=0
10190 FLAG%=0
10200 MD%=0
10210 CALL HRES (MD%,D%(0),FLAG%)
10220 IF FLAG%<>0 THEN PRINT "installation error":STOP
10230 RETURN
10240 '
10250 ' *****set up the sampeling rate
10260 '
10270 D%(0)=4
10280 D%(1)=SR2
10290 MD%=17
10300 CALL HRES (MD%,D%(0),FLAG%)
10310 IF FLAG%<>0 THEN PRINT "Mode 17-sampeling rate error":STOP
10320 '
10330 ' ******set up the scan limits
10340 '
10350 D%(0)=0
10360 D%(1)=2
10370 MD%=1
10380 CALL HRES (MD%,D%(0),FLAG%)
10390 IF FLAG%<>0 THEN PRINT "Mode 1-scan limit error":STOP
10400 '
10410 '
10420 '*********Sets up the Gains for the respective channels
10430 '
```

```
10440 D%(0)=G
10450 D%(1)=G2
10460 D%(2)=G2
10470 MD%=21
10480 CALL HRES(MD%,D%(0),FLAG%)
10490 '
10500 RETURN
10510 '
20000 '
20010 '***** SUBROUTINE TO MEASURE TEMPERATURE
20020 '
20030 '***program to initialize the dac
20040 '
20050 ' *****set up the sampeling rate
20060 '
20070 D%(0)=100
20080 D%(1)=1000
20090 MD%=17
20100 CALL HRES (MD%,D%(0),FLAG%)
20110 IF FLAG%<>0 THEN PRINT "Mode 17-sampeling rate  error":STOP
20120 '
20130 ' ******set up the scan limits
20140 '
20150 D%(0)=3
20160 D%(1)=3
20170 MD%=1
20180 CALL HRES (MD%,D%(0),FLAG%)
20190 IF FLAG%<>0 THEN PRINT "Mode 1-scan limit error":STOP
20200 '
20210 '*********Sets up the Gains for the respective  channels
20220 '
20230 D%(3)=2
20240 MD%=21
20250 CALL HRES(MD%,D%(0),FLAG%)
20260 '
20270 '*******Sample Temperature Directly
20280 '
20290 FOR I=1 TO 2
20300 MD%=3
20310 CALL HRES(MD%,D%(0),FLAG%)
20320 NEXT I
20330 TEMP1=D%(0)*(5/65536!)
20340 TEMP2=TEMP1*40
20350 LOCATE 7,40
```

```
20360 PRINT USING "##.#";TEMP2
20370 RETURN
30000 '
30010 '**** CONTINUOUS DATA COLLECTION
30020 '
30030 'mode 5A - first data acquisition
30040 '
30050 OPEN "o", #3, "c:\mccme\data\"+B$
30060 LOCATE 5,30
30070 PRINT TIME$
30080 D%(0)=N
30090 D%(1)=&H9000
30100 D%(2)=1
30110 D%(3)=0
30120 MD%=5
30130 CALL HRES (MD%,D%(0),FLAG%)
30140 IF FLAG%<>0 THEN GOTO  30140
30150 MD%=8
30160 CALL HRES(MD%,D%(0),FLAG%)
30170 IF D%(2)=N THEN GOTO 30200 ELSE GOTO 30150
30180 '*******retrieve the data using mode 9a
30190 '
30200 LOCATE 9,50
30210 PRINT TIME$
30220 D%(0)=N
30230 D%(1)=&H9000
30240 D%(2)=0
30250 D%(3)=VARPTR(DDA%(0))
30260 MD%=9
30270 CALL HRES (MD%,D%(0),FLAG%)
30280 IF FLAG%<>0 THEN PRINT "installation error":STOP
30290 A$=INKEY$
30300 IF A$="Q" OR A$="q" THEN GOTO 2700
30310 LOCATE 9,40
30320 PRINT CNTR
30330 CNTR=CNTR+1
30340 CNTR2=CNTR2+1
30350 '
30360 'mode 5b
30370 '
30380 D%(0)=N
30390 D%(1)=&H9000
30400 D%(2)=1
30410 D%(3)=0
```

```
30420 MD%=5
30430 CALL HRES (MD%,D%(0),FLAG%)
30440 IF FLAG%<>0 THEN GOTO 30440
30450 IF CNTR<=START THEN GOTO 30460 ELSE RETURN
30460 FOR I=0 TO NRND-1
30470 WRITE #3, DDA%(I)
30480 MD%=8
30490 CALL HRES(MD%,D%(0),FLAG%)
30500 IF D%(2)=N THEN GOTO 30550 ELSE GOTO 30510
30510 NEXT I
30520 MD%=8
30530 CALL HRES(MD%,D%(0),FLAG%)
30540 IF D%(2)=N THEN GOTO 30610 ELSE GOTO 30520
30550 PRINT "DATA TRANSFER TERMINATED AT N POINTS";I
30560 PRINT"You need to either select a smaller sampling rate or shorter
      scan"
30570 GOTO 240
30580 '
30590 '****Mode 9b
30600 '
30610 LOCATE 11,50
30620 PRINT TIME$
30630 D%(0)=N
30640 D%(1)=&H9000
30650 D%(2)=0
30660 D%(3)=VARPTR(DDB%(0))
30670 MD%=9
30680 CALL HRES (MD%,D%(0),FLAG%)
30690 IF FLAG%<>0 THEN PRINT "installation error":STOP
30700 A$=INKEY$
30710 IF A$="Q" OR A$="q" THEN GOTO 2700
30720 LOCATE 9,40
30730 PRINT CNTR
30740 CNTR=CNTR+1
30750 '
30760 '****Mode 5c
30770 '
30780 D%(0)=N
30790 D%(1)=&H9000
30800 D%(2)=1
30810 D%(3)=0
30820 MD%=5
30830 CALL HRES (MD%,D%(0),FLAG%)
30840 IF FLAG%<>0 THEN GOTO 30840
```

```
30850 IF CNTR< =START THEN GOTO 30860 ELSE RETURN
30860 FOR I=0 TO NRND-1
30870 WRITE #3, DDB%(I)
30880 MD%=8
30890 CALL HRES(MD%,D%(0),FLAG%)
30900 IF D%(2)=N THEN GOTO 30950 ELSE GOTO 30910
30910 NEXT I
30920 MD%=8
30930 CALL HRES(MD%,D%(0),FLAG%)
30940 IF D%(2)=N THEN GOTO 30200 ELSE GOTO 30920
30950 PRINT"Data transfer terminated at n points";I
30960 PRINT"You need to either select a smaller sampling rate or shorter
      scan"
30970 GOTO 240
40000 '
40010 '****** ONE SCAN OF DATA COLLECTION
40020 '
40030 ' Data collection
40040 '
40050 LOCATE 9,50
40060 PRINT TIME$
40070 D%(0)=N
40080 D%(1)=&H9000
40090 D%(2)=1
40100 D%(3)=0
40110 MD%=5
40120 CALL HRES (MD%,D%(0),FLAG%)
40130 MD%=8
40140 CALL HRES(MD%,D%(0),FLAG%)
40150 IF D%(2)=N THEN GOTO 40190 ELSE GOTO 40130
40160 '
40170 ' write time of scan to file
40180 '
40190 OPEN "c:\mccme\data\"+C$ FOR APPEND AS #1
40200 WRITE #1, CNTR;TIME$
40210 CLOSE #1
40220 '
40230 '*******retrieve the data using mode 9a
40240 '
40250 LOCATE 11,50
40260 PRINT TIME$
40270 D%(0)=N
40280 D%(1)=&H9000
40290 D%(2)=0
```

```
40300 D%(3)=VARPTR(DDA%(0))
40310 MD%=9
40320 CALL HRES (MD%,D%(0),FLAG%)
40330 IF FLAG%<>0 THEN PRINT "installation error":STOP
40340 A$=INKEY$
40350 IF A$="Q" OR A$="q" THEN GOTO 2710
40360 LOCATE 9,40
40370 PRINT CNTR
40380 CNTR=CNTR+XTH
40390 '
40400 OPEN "c:\mccme\data\"+B$ FOR APPEND AS #3
40410 FOR I=0 TO NRND-1
40420 WRITE #3, DDA%(I)
40430 NEXT I
40440 CLOSE #3
40450 '
40460 RETURN
40470 '
```

```
' 2wedatas.bas
' March 15, 1994
' Program for data manipulation of 2 WE system
' Lets user input the files to work on
' Gives user the option of extrapolating a baseline on the last scan of each
' Curve fits the data to a Gaussian shaped curve fit
' Subtracts the baseline from each scan if this has been specified
' Goes through each scan and picks out Ipc, Ratio, etc
' Saves all the data to the specified file names
' Does not save all of the smoothed data (huge files, long run time to do so)
'
CLS
NCHAN% = 3: SR2 = 5000: G = 3: G2 = 0: srate4 = 500: catmin = 0:
    anmax = .4
    vs = .8: vsw = -.2: scan = 500: amp2# = .00001:
    QCONV2 = 10: amp# = 9.96E-06: QCONV = 9.96: N2 = 4
'****This is where the user inputs the needed parameters for the program
'
PRINT : PRINT "THIS IS THE PROGRAM FOR TWO
     WORKING ELECTRODES"
PRINT "YOU CAN PERFORM A BASELINE SUBTRACTION"
PRINT "SMOOTH THE DATA, AND PICK OUT YOUR RELAVENT INFO"
'
PRINT : PRINT "These are the presumed settings:"
PRINT : PRINT "PLEASE NOTE THAT THESE SETTINGS WILL HOLD TRUE
FOR ALL FILES RUN"
PRINT : PRINT "Starting Voltage ="; vs
PRINT "Switching Voltage ="; vsw
PRINT "Scan rate = "; scan
PRINT "Scaling for CME (run through the I-E) = "; amp2#
PRINT "Scaling for the Bare Electrode (run through the Amp) ="; amp#
PRINT "Sampling rate = "; srate4
PRINT "Full Scale Voltage Range for the X Axis = 2.5 V"
PRINT "Full Scale Voltage Range for the Y Axis = 20 V"
PRINT "Voltage minima for the Peak Cathodic Current = "; catmin
PRINT "Voltage maxima for the Peak Anodic Current = "; anmax
PRINT : PRINT "If you used differnt settings you need to input them here"
PRINT "Do you need to change these settings? <y>"
300 a$ = INKEY$: IF a$ = "" THEN GOTO 300 ELSE GOTO 310
310 IF a$ = "Y" OR a$ = "y" THEN GOTO 320 ELSE GOTO 950
320 PRINT "Do you have the parameters you wish to use saved in a file?"
PRINT "Hit <y> if you do, otherwise hit anykey to continue"
340 a$ = INKEY$: IF a$ = "" THEN GOTO 340 ELSE GOTO 350
350 IF a$ = "Y" OR a$ = "y" THEN GOTO 360 ELSE GOTO 520
```

```
360 INPUT "Input the name of the file in which the parameters are saved:"; EXPS$
    OPEN "c:\mccme\expara\" + EXPS$ FOR INPUT AS #1
    INPUT #1, vs
    INPUT #1, vsw
    INPUT #1, scan
    INPUT #1, amp2#
    INPUT #1, QCONV2
    INPUT #1, amp#
    INPUT #1, QCONV
    INPUT #1, srate4
    INPUT #1, G
    INPUT #1, G2
    INPUT #1, N
    INPUT #1, npts%
    INPUT #1, catmin
    INPUT #1, anmax
    CLOSE #1
    GOTO 960
520 INPUT "Input your starting voltage (in Volts)"; vs
    INPUT "Input your switching voltage (in Volts)"; vsw
    INPUT "Input the scan rate you will be using (in mV/sec):"; scan
    XRNG = vs - vsw
    XSTP = (XRNG / 10)
    N2 = ((2 * XRNG) * (1 / (scan / 1000)))
    INPUT "Input the amplification for the CME (amp) (in amps/volt):"; amp2#
    QCONV2 = (amp2# / .000001)
    INPUT "Input the amplification for the Bare Electrode (I-E) (in amps/volt):";
        amp#
    QCONV = (amp# / .000001)
    PRINT : PRINT "A single scan will take x seconds. x="; N2
    PRINT "Did you change the sampling rate? If so hit <y>"
640 a$ = INKEY$: IF a$ = "" THEN GOTO 640 ELSE GOTO 650
650 IF a$ = "Y" OR a$ = "y" THEN GOTO 660 ELSE GOTO 750
660 INPUT "Input the sampling rate you used"; SRATE
    SRATE2 = INT(10000000# / SRATE)
    SR2 = INT(SRATE2 / 4)
    SRATE3 = (4 * SR2)
    srate4 = (10000000# / SRATE3)
    PRINT "Actual sampling rate is:"; srate4
    PRINT "If this is acceptable hit <Y>"
730 a$ = INKEY$: IF a$ = "" THEN GOTO 730 ELSE GOTO 740
740 IF a$ = "Y" OR a$ = "y" GOTO 750 ELSE GOTO 660
750 NTEMP = INT(N2 * srate4)
    NTEMP2 = INT(NTEMP / 3)
```

```
   N = NTEMP2 * 3
   IF N > 10000 THEN GOTO 790 ELSE GOTO 800
790 PRINT "Your Number of Points/Scan is too high.  You need to choose a slower
       rate": GOTO 660
800 npts% = N / NCHAN%
   PRINT : PRINT "The default scaling for the X Axis is 2.5 V full scale"
   PRINT : PRINT "The default scaling for the Y Axis is 20 V full scale"
   PRINT "Did you change the scaling? If so hit <y>"
840 a$ = INKEY$: IF a$ = "" THEN GOTO 840 ELSE GOTO 850
850 IF a$ = "Y" OR a$ = "y" THEN GOTO 860 ELSE GOTO 900
860 PRINT "You can change the scaling for the voltage and current as
       follows:"
   PRINT "To get a Full Scale Voltage of:  CHOOSE:"
   PRINT "                          20V     0"
   PRINT "                          10V     1"
   PRINT "                           5V     2"
   PRINT "                         2.5V     3"
   PRINT : INPUT "Enter the scaling used (choose 0-3) for the Potential:"; G
   INPUT "Enter the scaling used (choose 0-3) for the working electrodes:";
       G2
900 INPUT "Enter the minimum voltage at which the peak cathodic current
      will be seen:"; catmin
   INPUT "Enter the maximum voltage at which the peak anodic current will
       be seen:"; anmax
   GOTO 960
950 vs = .8: vsw = -.2: scan = 500: amp2# = .00001:
      QCONV2 = 10: amp# = 9.96E-06: QCONV = 9.96: N2 = 4
960 XRNG = vs - vsw
   XSTP = (XRNG / 10)
   N2 = ((2 * XRNG) * (1 / (scan / 1000)))
   NTEMP = N2 * srate4
   NTEMP2 = INT(NTEMP / 3)
    N = NTEMP2 * 3
    npts% = N / NCHAN%
    half = INT(npts% / 2)
1020 IF iFILES > 1 THEN GOTO 1040 ELSE GOTO 1030
1030 DIM DDA%(N), SORT(npts%, 3), fit(npts%, 3)
    qmax = 0: qmin = 0: qmax2 = 0: qmin2 = 0: qmxbr = 0: qmnbr = 0
    eqmn = 0: eqmx = 0: eqmn2 = 0: eqmx2 = 0: RMAX = 0
    COUNTER = 1
    '
    ' ***Sets up the conversions for data and graphing
    '
1040 IF G = 0 THEN conv = (20 / 65536!)
```

```
    IF G = 1 THEN conv = (10 / 65536!)
    IF G = 2 THEN conv = (5 / 65536!)
    IF G = 3 THEN conv = (2.5 / 65536!)
    IF G2 = 0 THEN CONV2 = (20 / 65536!)
    IF G2 = 1 THEN CONV2 = (10 / 65536!)
    IF G2 = 2 THEN CONV2 = (5 / 65536!)
    IF G2 = 3 THEN CONV2 = (2.5 / 65536!)
    X1 = INT(-vs / (conv))
    X2 = INT(-vsw / (conv))
    Y1 = 8
    Y2 = 632
    xmean = (X2 + X1) / 2
    ymean = (Y2 + Y1) / 2
    a2 = ((X1 - xmean) ^ 2) + ((X2 - xmean) ^ 2)
    b2 = ((Y1 - ymean) ^ 2) + ((Y2 - ymean) ^ 2)
    AB = ((X2 - xmean) * (Y2 - ymean)) + ((X1 - xmean) * (Y1 - ymean))
    SLOPE = AB / a2
    YINT = ymean - (SLOPE * xmean)
    catminb = catmin / conv
    anmaxb = anmax / conv
    '
   INPUT "How many files do you want to run?"; NFILES
   FOR iFILES = 1 TO NFILES
   CLS
   PRINT "The most recent experiments were saved as:"
   OPEN "c:\mccme\data\exps" FOR INPUT AS #2
1330 IF EOF(2) GOTO 1390
    LINE INPUT #2, EX$
    PRINT "File name"; EX$
    LINE INPUT #2, CN$
    PRINT "Number of scans in file  "; CN$
    GOTO 1330
1390 CLOSE #2
    PRINT "You can choose these files or any others"
    OPEN "c:\mccme\data\files" FOR APPEND AS #1
    PRINT "Input the name of the"; iFILES: INPUT "file"; fl$
    INPUT "Input the number of scans contained in the file:"; cntr
    PRINT #1, fl$
    PRINT #1, cntr
    PRINT #1, cntr
    INPUT "Input the filename for the last scan of the smoothed data"; SML$
    PRINT #1, SML$
    INPUT "Input the name of the file to which the Ratio information will be
        saved"; RT$
```

```
    PRINT #1, RT$
    INPUT "Input the name of the file to which the Ipc and ratio info will be
        saved"; CU$
    PRINT #1, CU$
    CLOSE #1
    '
    ' ***Extropolate Baseline?
    '
    PRINT "Do you want to extrapolate a baseline for this file? <y>"
1620 a$ = INKEY$: IF a$ = "" GOTO 1620
    IF a$ = "y" OR a$ = "Y" GOTO 1640 ELSE GOTO 1630
1630 cmeslope = 0: cmeyint = 0: bareslope = 0: bareyint = 0
    cmeslope2 = 0: cmeyint2 = 0: bareslope2 = 0:
        bareyint2 = 0
    GOTO 2860
    '
    ' Baseline Extrapolation
    '
1640 OPEN "c:\mccme\data\" + fl$ FOR INPUT AS #1
    CLS : SCREEN 2
    PRINT "Is there a specific scan you want to begin evaluating for baseline
        extrapolation <y>?"
1740 a$ = INKEY$: IF a$ = "" GOTO 1740
    IF a$ = "y" OR a$ = "Y" THEN GOTO 1750 ELSE GOTO 1760
1750 INPUT "Enter the number of the scan at which you wish to begin
        evaluation"; cntr
    mc = 1: m = 1: cntr2 = 1
    '
    '***Program to input a scan for the extrapolation
    '
1760 CLS
    IF EOF(1) THEN GOTO 2854 ELSE GOTO 1765
1765 IF m > 1 THEN AF = 3 ELSE AF = 0
    FOR i = (0 + AF) TO N - 2 STEP 3
    ii = i / 3
    j = i + 1
    K = j + 1
    INPUT #1, DDA%(i)
    IF EOF(1) THEN GOTO 2854
    INPUT #1, DDA%(j)
    IF EOF(1) THEN GOTO 2854
    INPUT #1, DDA%(K)
    IF EOF(1) THEN GOTO 2854
    fit(ii, 0) = DDA%(i)
```

```
    fit(ii, 1) = DDA%(j)
    fit(ii, 2) = DDA%(K)
    NEXT i
    IF mc = 1 THEN GOTO 1770 ELSE GOTO 1800
1770 cntr2 = cntr2 + 1
    PRINT cntr2
    IF cntr2 = cntr - 1 THEN GOTO 1800 ELSE GOTO 1765
    '
    'Extraploate the baseline
    '
1800 CLS
    y = 0
    z = 100
1830 sumx = 0
    sumx2 = 0
    sumy = 0
    sumy2 = 0
    sumxy = 0
    FOR i = y TO z
    sumx = sumx + fit(i, 0)
    sqrx = (fit(i, 0) ^ 2)
    sumx2 = sumx2 + sqrx
    sumy = sumy + fit(i, 1)
    sqry = (fit(i, 1) ^ 2)
    sumy2 = sumy2 + sqry
    sumxy = sumxy + (fit(i, 0) * fit(i, 1))
    NEXT i
    div2 = INT(z - y)
    xmean = (sumx / div2)
    ymean = (sumy / div2)
    a2 = (sumx2 - ((sumx ^ 2) / div2))
    b2 = (sumy2 - ((sumy ^ 2) / div2))
    AB = (sumxy - ((sumx * sumy) / div2))
    cmeslope = AB / a2
    cmeyint = ymean - (cmeslope * xmean)
    '
    X = YINT + ((fit(y, 0) * SLOPE) * -1)
    Y1 = (100 - ((fit(y, 1) * CONV2 * 10) * QCONV2))
    PSET (X, Y1)
    FOR i = 0 TO half
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
    Y1 = (100 - ((fit(i, 1) * CONV2 * 10) * QCONV2))
    LINE -(X, Y1)
    NEXT i
```

```
    '
    bline = (cmeslope * fit(y, 0)) + cmeyint
    X = YINT + ((fit(y, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2))
    PSET (X, Y1)
    FOR i = 0 TO half
    bline = (cmeslope * fit(i, 0)) + cmeyint
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2))
    LINE -(X, Y1)
    NEXT i
    '
    LOCATE 5, 5
    PRINT "This is the extrapolated baseline for the CME, is it acceptable?"
1930 a$ = INKEY$: IF a$ = "" GOTO 1930
    IF a$ = "y" OR a$ = "Y" THEN GOTO 2000 ELSE GOTO 1950
1950 PRINT "The current length of the baseline is"; y; "to"; z
    INPUT "Enter the new starting point for the baseline"; y$
    INPUT "Enter the new stopping point for the baseline"; z$
    y = VAL(y$): z = VAL(z$)
    CLS : GOTO 1830
    '
2000 w = y: V = z
    CLS
2020 sumx = 0
    sumx2 = 0
    sumy = 0
    sumy2 = 0
    sumxy = 0
    FOR i = w TO V
    sumx = sumx + fit(i, 0)
    sqrx = (fit(i, 0) ^ 2)
    sumx2 = sumx2 + sqrx
    sumy = sumy + fit(i, 2)
    sqry = (fit(i, 2) ^ 2)
    sumy2 = sumy2 + sqry
    sumxy = sumxy + (fit(i, 0) * fit(i, 2))
    NEXT i
    div2 = INT(V - w)
    xmean = (sumx / div2)
    ymean = (sumy / div2)
    a2 = (sumx2 - ((sumx ^ 2) / div2))
    b2 = (sumy2 - ((sumy ^ 2) / div2))
    AB = (sumxy - ((sumx * sumy) / div2))
```

```
    bareslope = AB / a2
    bareyint = ymean - (bareslope * xmean)
    '
    X = YINT + ((fit(w, 0) * SLOPE) * -1)
    Y2 = (100 - ((fit(w, 2) * CONV2 * 10) * QCONV))
    PSET (X, Y2)
    FOR i = 0 TO half
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
    Y2 = (100 - ((fit(i, 2) * CONV2 * 10) * QCONV))
    LINE -(X, Y2)
    NEXT i
    '
    bline = (bareslope * fit(w, 0)) + bareyint
    X = YINT + ((fit(w, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2))
    PSET (X, Y1)
    FOR i = 0 TO half
    bline = (bareslope * fit(i, 0)) + bareyint
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2))
    LINE -(X, Y1)
    NEXT i
    '
    LOCATE 5, 5
    PRINT "This is the extrapolated baseline for the bare electrode, is it
        acceptable?"
2120 a$ = INKEY$: IF a$ = "" GOTO 2120 ELSE GOTO 2130
2130 IF a$ = "y" OR a$ = "Y" THEN GOTO 2190 ELSE GOTO 2140
2140 PRINT "The current length of the baseline is"; w; "to"; V
    INPUT "Enter the new starting point for the baseline"; w$
    INPUT "Enter the new stopping point for the baseline"; V$
    w = VAL(w$): V = VAL(V$)
    CLS : GOTO 2020
    '
2190 CLS
    q = 0: r = 100
2210 q2 = q + half: r2 = r + half
    sumx = 0
    sumx2 = 0
    sumy = 0
    sumy2 = 0
    sumxy = 0
    FOR i = q2 TO r2
    sumx = sumx + fit(i, 0)
```

```
    sqrx = (fit(i, 0) ^ 2)
    sumx2 = sumx2 + sqrx
    sumy = sumy + fit(i, 1)
    sqry = (fit(i, 1) ^ 2)
    sumy2 = sumy2 + sqry
    sumxy = sumxy + (fit(i, 0) * fit(i, 1))
    NEXT i
    div2 = INT(r2 - q2)
    xmean = (sumx / div2)
    ymean = (sumy / div2)
    a2 = (sumx2 - ((sumx ^ 2) / div2))
    b2 = (sumy2 - ((sumy ^ 2) / div2))
    AB = (sumxy - ((sumx * sumy) / div2))
    cmeslope2 = AB / a2
    cmeyint2 = ymean - (cmeslope2 * xmean)
    '
    X = YINT + ((fit(q2, 0) * SLOPE) * -1)
    Y1 = (100 - ((fit(q2, 1) * CONV2 * 10) * QCONV2))
    PSET (X, Y1)
    FOR i = half TO npts% - 1
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
    Y1 = (100 - ((fit(i, 1) * CONV2 * 10) * QCONV2))
    LINE -(X, Y1)
    NEXT i
    '
    bline = (cmeslope2 * fit(q2, 0)) + cmeyint2
    X = YINT + ((fit(q2, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2))
    PSET (X, Y1)
    FOR i = half TO npts% - 1
    bline = (cmeslope2 * fit(i, 0)) + cmeyint2
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2))
    LINE -(X, Y1)
    NEXT i
    '
    LOCATE 5, 5
    PRINT "This is the extrapolated return baseline for the CME, is it
        acceptable?"
2320 a$ = INKEY$: IF a$ = "" GOTO 2320 ELSE GOTO 2330
2330 IF a$ = "y" OR a$ = "Y" THEN GOTO 2390 ELSE GOTO 2340
2340 PRINT "The current length of the baseline is"; q;
        "to"; r
2342 INPUT "Enter the new starting point for the baseline"; q$
```

```
    q = VAL(q$)
    IF q > 350 THEN
    PRINT "Value too large-Select smaller": GOTO 2342
    ELSEIF q <= 350 THEN GOTO 2343
    END IF
2343 INPUT "Enter the new stopping point for the baseline"; r$
    r = VAL(r$)
    IF r > 350 THEN
    PRINT "Value too large-Select smaller": GOTO 2343
    ELSEIF r <= 350 THEN GOTO 2344
    END IF
2344 CLS : GOTO 2210
    '
2390 CLS
    s = q: t = r
2410 s2 = s + half: t2 = t + half
    sumx = 0
    sumx2 = 0
    sumy = 0
    sumy2 = 0
    sumxy = 0
    FOR i = s2 TO t2
    sumx = sumx + fit(i, 0)
    sqrx = (fit(i, 0) ^ 2)
    sumx2 = sumx2 + sqrx
    sumy = sumy + fit(i, 2)
    sqry = (fit(i, 2) ^ 2)
    sumy2 = sumy2 + sqry
    sumxy = sumxy + (fit(i, 0) * fit(i, 2))
    NEXT i
    div2 = INT(t - s)
    xmean = (sumx / div2)
    ymean = (sumy / div2)
    a2 = (sumx2 - ((sumx ^ 2) / div2))
    b2 = (sumy2 - ((sumy ^ 2) / div2))
    AB = (sumxy - ((sumx * sumy) / div2))
    bareslope2 = AB / a2
    bareyint2 = ymean - (bareslope2 * xmean)
    '
    X = YINT + ((fit(s2, 0) * SLOPE) * -1)
    Y2 = (100 - ((fit(s2, 2) * CONV2 * 10) * QCONV))
    PSET (X, Y2)
    FOR i = half TO npts% - 1
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
```

```
    Y2 = (100 - ((fit(i, 2) * CONV2 * 10) * QCONV))
    LINE -(X, Y2)
    NEXT i
    '
    bline = (bareslope2 * fit(s2, 0)) + bareyint2
    X = YINT + ((fit(s2, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2))
    PSET (X, Y1)
    FOR i = half TO npts% - 1
    bline = (bareslope2 * fit(i, 0)) + bareyint2
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2))
    LINE -(X, Y1)
    NEXT i
    '
    LOCATE 5, 5
    PRINT "This is the extrapolated return baseline for the bare electrode,
       is it acceptable?"
2520 a$ = INKEY$: IF a$ = "" GOTO 2520
    IF a$ = "y" OR a$ = "Y" THEN GOTO 2590 ELSE GOTO 2540
2540 PRINT "The current length of the baseline is"; s;"to"; t
2542 INPUT "Enter the new starting point for the baseline"; s$
    s = VAL(s$)
    IF s > 350 THEN
    PRINT "Value too large-Select smaller": GOTO 2542
    ELSEIF s <= 350 THEN GOTO 2543
    END IF
2543 INPUT "Enter the new stopping point for the baseline"; t$
    t = VAL(t$)
    IF t > 350 THEN
    PRINT "Value too large-Select smaller": GOTO 2543
    ELSEIF t <= 350 THEN GOTO 2544
    END IF
2544 CLS : GOTO 2410
    '
2590 mc = 0
    PRINT "Do you want to extrapolate for the next scan instead?"
2852 a$ = INKEY$: IF a$ = "" THEN GOTO 2852
    IF a$ = "Y" OR a$ = "y" THEN GOTO 1760 ELSE GOTO 2854
2854 CLOSE #1
2860 OPEN "c:\mccme\data\files" FOR APPEND AS #2
    WRITE #2, cmeslope
    WRITE #2, cmeyint
    WRITE #2, bareslope
```

```
    WRITE #2, bareyint
    WRITE #2, cmeslope2
    WRITE #2, cmeyint2
    WRITE #2, bareslope2
    WRITE #2, bareyint2
    CLOSE #2
2880 NEXT iFILES
    '
    '****Actual loop of the program
    '
2890 CLS
    '
    ' open files and set up screen display
    '
    LOCATE 3, 5
    PRINT "Number of Files to Work on is:"; NFILES
    OPEN "c:\mccme\data\files" FOR INPUT AS #1
    FOR NF = 1 TO NFILES
    LOCATE 5, 5
    PRINT "Currently Working on Number:"; NF
    INPUT #1, fl$
    INPUT #1, cntr
    INPUT #1, SM$
    INPUT #1, SML$
    INPUT #1, RT$
    INPUT #1, CU$
    INPUT #1, cmeslope
    INPUT #1, cmeyint
    INPUT #1, bareslope
    INPUT #1, bareyint
    INPUT #1, cmeslope2
    INPUT #1, cmeyint2
    INPUT #1, bareslope2
    INPUT #1, bareyint2
    LOCATE 7, 5
    PRINT "Name of File which is currently being worked on is:"; fl$
    LOCATE 9, 5
    PRINT "Number of scans evaluated from file:"
    LOCATE 11, 5
    PRINT "Number of points evaluated from scan:"
    OPEN "c:\mccme\data\" + fl$ FOR INPUT AS #2
    OPEN "c:\mccme\data\" + CU$ FOR APPEND AS #3
    WRITE #3, "scan#", "Time", "Ratio"
    WRITE #3, "Ipcc", "Ibare", "Epcc", "Ipac", "Ibare", "Epac"
```

```
    WRITE #3, "Ipcb", "Epcb", "Ipab", "Epab"
    CLOSE #3
    m = 0
3160 m = m + 1
    LOCATE 9, 50
    PRINT m
    IF m > 1 THEN AF = 3 ELSE AF = 0
    FOR i = (0 + AF) TO N - 2 STEP 3
    ii = i / 3
    j = i + 1
    K = j + 1
    IF EOF(2) THEN GOTO 4360 ELSE GOTO 3250
3250 INPUT #2, DDA%(i)
    IF EOF(2) THEN GOTO 4360 ELSE GOTO 3270
3270 INPUT #2, DDA%(j)
    IF EOF(2) THEN GOTO 4360 ELSE GOTO 3290
3290 INPUT #2, DDA%(K)
    SORT(ii, 0) = DDA%(i)
    SORT(ii, 1) = DDA%(j)
    SORT(ii, 2) = DDA%(K)
    NEXT i
    FOR i = 11 TO (npts% - 10)
    j = i - 11
    LOCATE 11, 50
    PRINT j
    ZERO = 329 * (SORT(i, 0))
    ONE = 324 * (SORT((i + 1), 0) + SORT((i - 1), 0))
    TWO = 309 * (SORT((i + 2), 0) + SORT((i - 2), 0))
    THREE = 284 * (SORT((i + 3), 0) + SORT((i - 3), 0))
    FOUR = 249 * (SORT((i + 4), 0) + SORT((i - 4), 0))
    FIVE = 204 * (SORT((i + 5), 0) + SORT((i - 5), 0))
    SIX = 149 * (SORT((i + 6), 0) + SORT((i - 6), 0))
    SEVEN = 84 * (SORT((i + 7), 0) + SORT((i - 7), 0))
    EIGHT = 9 * (SORT((i + 8), 0) + SORT((i - 8), 0))
    NINE = -76 * (SORT((i + 9), 0) + SORT((i - 9), 0))
    TEN = -171 * (SORT((i + 10), 0) + SORT((i - 10), 0))
    fit(j, 0) = (ZERO + ONE + TWO + THREE + FOUR + FIVE +SIX +
        SEVEN + EIGHT + NINE + TEN) / 3059
    ZERO = 329 * (SORT(i, 1))
    ONE = 324 * (SORT((i + 1), 1) + SORT((i - 1), 1))
    TWO = 309 * (SORT((i + 2), 1) + SORT((i - 2), 1))
    THREE = 284 * (SORT((i + 3), 1) + SORT((i - 3), 1))
    FOUR = 249 * (SORT((i + 4), 1) + SORT((i - 4), 1))
    FIVE = 204 * (SORT((i + 5), 1) + SORT((i - 5), 1))
```

```
    SIX = 149 * (SORT((i + 6), 1) + SORT((i - 6), 1))
    SEVEN = 84 * (SORT((i + 7), 1) + SORT((i - 7), 1))
    EIGHT = 9 * (SORT((i + 8), 1) + SORT((i - 8), 1))
    NINE = -76 * (SORT((i + 9), 1) + SORT((i - 9), 1))
    TEN = -171 * (SORT((i + 10), 1) + SORT((i - 10), 1))
    fit(j, 1) = (ZERO + ONE + TWO + THREE + FOUR + FIVE +SIX +
        SEVEN + EIGHT + NINE + TEN) / 3059
    ZERO = 329 * (SORT(i, 2))
    ONE = 324 * (SORT((i + 1), 2) + SORT((i - 1), 2))
    TWO = 309 * (SORT((i + 2), 2) + SORT((i - 2), 2))
    THREE = 284 * (SORT((i + 3), 2) + SORT((i - 3), 2))
    FOUR = 249 * (SORT((i + 4), 2) + SORT((i - 4), 2))
    FIVE = 204 * (SORT((i + 5), 2) + SORT((i - 5), 2))
    SIX = 149 * (SORT((i + 6), 2) + SORT((i - 6), 2))
    SEVEN = 84 * (SORT((i + 7), 2) + SORT((i - 7), 2))
    EIGHT = 9 * (SORT((i + 8), 2) + SORT((i - 8), 2))
    NINE = -76 * (SORT((i + 9), 2) + SORT((i - 9), 2))
    TEN = -171 * (SORT((i + 10), 2) + SORT((i - 10), 2))
    fit(j, 2) = (ZERO + ONE + TWO + THREE + FOUR + FIVE +SIX +
        SEVEN + EIGHT + NINE + TEN) / 3059
    '
    ' Picking out the peak info
    '
3840 IF fit(j, 0) < catminb THEN GOTO 3880
    IF qmax2 < fit(j, 1) THEN GOTO 3850 ELSE GOTO 3880
3850 qmax2 = fit(j, 1)
    eqmx2 = fit(j, 0)
    qmxbr = fit(j, 2)
3880 IF fit(j, 0) > anmaxb THEN GOTO 3920
    IF qmin2 > fit(j, 1) THEN GOTO 3890 ELSE GOTO 3920
3890 qmin2 = fit(j, 1)
    eqmn2 = fit(j, 0)
    qmnbr = fit(j, 2)
3920 IF fit(j, 0) < catminb THEN GOTO 3950
    IF qmax < fit(j, 2) THEN GOTO 3930 ELSE GOTO 3950
3930 qmax = fit(j, 2)
    eqmx = fit(j, 0)
3950 IF fit(j, 0) > anmaxb THEN GOTO 3980
    IF qmin > fit(j, 2) THEN GOTO 3960 ELSE GOTO 3980
3960 qmin = fit(j, 2)
    eqmn = fit(j, 0)
3980 IF COUNTER = (cntr - 1) THEN GOTO 4020 ELSE GOTO 4050
4020 OPEN "c:\mccme\data\" + SML$ FOR APPEND AS #3
    WRITE #3, fit(j, 0), fit(j, 1), fit(j, 2)
```

```
    CLOSE #3
4050 NEXT i
    '**** Subtracts the extrapolated baseline, Converts
    'the data to real #'s, and writes to disc
    '
    cmebase = (cmeslope * eqmx2) + cmeyint
    barebase = (bareslope * eqmx) + bareyint
    cmebase2 = (cmeslope2 * eqmn2) + cmeyint2
    barebase2 = (bareslope2 * eqmn) + bareyint2
    '
    qmax2 = qmax2 - cmebase
    qmax2 = (qmax2 * CONV2) * amp2#
    '
    qmin2 = qmin2 - cmebase2
    qmin2 = (qmin2 * CONV2) * amp2#
    '
    qmxbr = qmxbr - barebase
    qmxbr = (qmxbr * CONV2) * amp#
    '
    qmnbr = qmnbr - barebase2
    qmnbr = (qmnbr * CONV2) * amp#
    '
    eqmx2 = (eqmx2 * conv)
    eqmn2 = (eqmn2 * conv)
    '
    qmax = qmax - barebase
    qmax = (qmax * CONV2) * amp#
    '
    qmin = qmin - barebase2
    qmin = (qmin * CONV2) * amp#
    '
    eqmx = (eqmx * conv)
    eqmn = (eqmn * conv)
    '
    time = m * N2
    IF qmax = 0 THEN RATIO = 0 ELSE RATIO = (qmax2 / qmax)
    '
    OPEN "c:\mccme\data\" + RT$ FOR APPEND AS #3
    PRINT #3, USING "##.##"; time; RATIO
    CLOSE #3
    OPEN "c:\mccme\data\" + CU$ FOR APPEND AS #3
    PRINT #3, USING "##.##"; m; time; RATIO
    PRINT #3, USING "##.##^^^^"; qmax2; qmxbr; eqmx2; qmin2; qmnbr;
        eqmn2
```

```
    PRINT #3, USING "##.##^^^^"; qmax; eqmx; qmin; eqmn
    CLOSE #3
    qmax = 0: qmin = 0: qmax2 = 0: qmin2 = 0
    COUNTER = COUNTER + 1
    GOTO 3160
4360 CLOSE #2
    COUNTER = 1
    NEXT NF
    CLOSE #1
    CLS
    END
```

```
   ' 2wegraph.bas
   ' March 15, 1994
   ' Program for data manipulation of 2 WE system
   ' Lets user input the files to work on
   ' Gives user the option of extrapolating a baseline on the last scan of each
   ' Gives user the option of graphing the scans or the ratio data
   ' Gives user the option of printing the current info
   '
   NCHAN% = 3: SR2 = 5000: G = 3: G2 = 0: srate4 = 500: cycles = 0:
        scale = 1
90 CLS
   '
   PRINT "THIS IS THE PROGRAM FOR 2 WORKING ELECTRODE
        DATA MANIPULATION"
   PRINT "IN ORDER TO PRINT THE RATIO AND CURRENT
        INFORMATION YOU MUST FIRST USE 2WEDATA"
   PRINT "YOU DO NOT NEED TO PERFORM PREVIOUS OPERATIONS F O R
THE SCANS"
   PRINT : PRINT "Choose an option:"
   PRINT "1. Input the name of the files to use"
   PRINT "2. Graph a scan showing the extraplated baseline"
   PRINT "3. Graph the last scan"
   PRINT "4. Graph every X scan"
   PRINT "5. Graph all scans"
   PRINT "6. Graph ratio vs time"
   PRINT "7. Print the Ratio and Current Information"
   PRINT "8. Quit"
230 z$ = INKEY$: IF z$ = "" THEN GOTO 230 ELSE GOTO 240
240 z = VAL(z$)
   ON z GOTO 290, 2002, 3450, 4130, 4780, 5310, 5720, 6100
   '
   'Routine to input the file
   '
290 CLS
   PRINT : PRINT "These are the presumed settings:"
   PRINT : PRINT "Starting Voltage = "; vs
   PRINT "Switching Voltage = "; vsw
   PRINT "Scan rate = "; scan
   PRINT "Scaling for CME (run through the Amp) = "; amp2#
   PRINT "Scaling for the Bare Electrode (run through the I-E) = "; amp#
   PRINT "Sampling rate = "; srate4
   PRINT "Full Scale Voltage Range for the X Axis= 2.5 V"
   PRINT "Full Scale Voltage Range for the Y Axis= 20 V"
   PRINT : PRINT "If you used different setting you need to input them here"
```

```
   PRINT "Do you need to change these settings? <y>"
420 a$ = INKEY$: IF a$ = "" THEN GOTO 420 ELSE GOTO 430
430 IF a$ = "Y" OR a$ = "y" THEN GOTO 500 ELSE GOTO 1430
500 PRINT "Do you have the parameters you wish to use saved in a file?"
   PRINT "Hit <y> if you do, otherwise hit anykey to continue"
520 a$ = INKEY$: IF a$ = "" THEN GOTO 520 ELSE GOTO 530
530 IF a$ = "Y" OR a$ = "y" THEN GOTO 540 ELSE GOTO 1000
540 INPUT "Input the name of the file in which the parameters are saved:"; EXPS$
   OPEN "c:\mccme\expara\" + EXPS$ FOR INPUT AS #1
   INPUT #1, vs
   INPUT #1, vsw
   INPUT #1, scan
   INPUT #1, amp2#
   INPUT #1, QCONV2
   INPUT #1, amp#
   INPUT #1, QCONV
   INPUT #1, srate4
   INPUT #1, G
   INPUT #1, G2
   INPUT #1, N
   INPUT #1, npts%
   INPUT #1, catmin
   INPUT #1, anmax
   CLOSE #1
   GOTO 1440
1000 INPUT "Input your starting voltage (in Volts)"; vs
    INPUT "Input your switching voltage (in Volts)"; vsw
    INPUT "Input the scan rate you will be using
       (in mV/sec):"; scan
    XRNG = vs - vsw
    XSTP = (XRNG / 10)
    N2 = ((2 * XRNG) * (1 / (scan / 1000)))
    INPUT "Input the amplification for the CME (amp)
       (in amps/volt):"; amp2#
    QCONV2 = (amp2# / .000001)
    INPUT "Input the amplification for the Bare Electrode (I-E) (in amps/volt):"; amp#
    QCONV = (amp# / .000001)
    PRINT : PRINT "A single scan is calculated to take x seconds. x="; N2
    PRINT "Did you change the sampling rate? If so hit <y>"
1120 a$ = INKEY$: IF a$ = "" THEN GOTO 1120 ELSE GOTO 1130
1130 IF a$ = "Y" OR a$ = "y" THEN GOTO 1140 ELSE GOTO 1230
1140 INPUT "Input the sampling rate you used"; SRATE
    sRATE2 = INT(10000000# / SRATE)
    SR2 = INT(sRATE2 / 4)
```

```
    SRATE3 = (4 * SR2)
    srate4 = (10000000# / SRATE3)
    PRINT "Actual sampling rate is:"; srate4
    PRINT "If this is acceptable hit <Y>"
1210 a$ = INKEY$: IF a$ = "" THEN GOTO 1210 ELSE GOTO 1220
1220 IF a$ = "Y" OR a$ = "y" GOTO 1230 ELSE GOTO 1140
1230 NTEMP = INT(N2 * srate4)
    NTEMP2 = INT(NTEMP / 3)
    N = NTEMP2 * 3
    IF N > 10000 THEN GOTO 1270 ELSE GOTO 1280
1270 PRINT "Your Number of Points/Scan is too high.  You need to choose a slower
rate": GOTO 1140
1280 npts% = N / NCHAN%
    PRINT : PRINT "The default scaling for the X Axis is 2.5 V full scale"
    PRINT : PRINT "The default scaling for the Y Axis is 20 V full scale"
    PRINT "Did you change the scaling? If so hit <y>"
1320 a$ = INKEY$: IF a$ = "" THEN GOTO 1320 ELSE GOTO 1330
1330 IF a$ = "Y" OR a$ = "y" THEN GOTO 1340 ELSE GOTO 1510
1340 PRINT "You can change the scaling for the voltage and current as follows:"
    PRINT "To get a Full Scale Voltage of:  CHOOSE:"
    PRINT "                          20V     0"
    PRINT "                          10V     1"
    PRINT "                           5V     2"
    PRINT "                         2.5V     3"
    PRINT : INPUT "Enter the scaling used (choose 0-3) for the Potential:"; G
    INPUT "Enter the scaling used (choose 0-3) for the working
       electrodes:"; G2
    GOTO 1440
1430 IF cycles = 1 THEN GOTO 1865 ELSE GOTO 1435
1435 vs = .8: vsw = -.2: scan = 500: amp2# = .00001: QCONV2 = 10:
       amp# = 9.96E-06: QCONV = 9.96: N2 = 4
1440 XRNG = vs - vsw
    XSTP = (XRNG / 10)
    N2 = ((2 * XRNG) * (1 / (scan / 1000)))
    NTEMP = N2 * srate4
    NTEMP2 = INT(NTEMP / 3)
    N = NTEMP2 * 3
    npts% = N / NCHAN%
    half = INT(npts% / 2)
1510 QMAX = 0: QMIN = 0: QMAX2 = 0: QMIN2 = 0: QMXBR = 0:
       QMNBR = 0
    EQMN = 0: EQMX = 0: EQMN2 = 0: EQMX2 = 0: rmax = 0
    USED = 0
    IF cycles = 1 THEN GOTO 1590 ELSE GOTO 1550
```

```
1550 DIM DDA%(N), fit(npts%, 3)
     '
     ' ***Sets up the conversions for data and graphing
     '
1590 IF G = 0 THEN CONV = (20 / 65536!)
     IF G = 1 THEN CONV = (10 / 65536!)
     IF G = 2 THEN CONV = (5 / 65536!)
     IF G = 3 THEN CONV = (2.5 / 65536!)
     IF G2 = 0 THEN CONV2 = (20 / 65536!)
     IF G2 = 1 THEN CONV2 = (10 / 65536!)
     IF G2 = 2 THEN CONV2 = (5 / 65536!)
     IF G2 = 3 THEN CONV2 = (2.5 / 65536!)
     X1 = INT(-vs / (CONV))
     x2 = INT(-vsw / (CONV))
     Y1 = 8
     y2 = 632
     xmean = (x2 + X1) / 2
     ymean = (y2 + Y1) / 2
     a2 = ((X1 - xmean) ^ 2) + ((x2 - xmean) ^ 2)
     b2 = ((Y1 - ymean) ^ 2) + ((y2 - ymean) ^ 2)
     AB = ((x2 - xmean) * (y2 - ymean)) + ((X1 - xmean) * (Y1 - ymean))
     SLOPE = AB / a2
     YINT = ymean - (SLOPE * xmean)
     '
     ' Actual input of the data
     '
     CLS
     '
1865 OPEN "c:\mccme\data\files" FOR INPUT AS #1
1860 IF EOF(1) GOTO 1900
     INPUT #1, org$
     INPUT #1, nu
     INPUT #1, sc$
     INPUT #1, scl$
     INPUT #1, rt$
     INPUT #1, ip$
     INPUT #1, cmeslope
     INPUT #1, cmeyint
     INPUT #1, bareslope
     INPUT #1, bareyint
     INPUT #1, cmeslope2
     INPUT #1, cmeyint2
     INPUT #1, bareslope2
     INPUT #1, bareyint2
```

```
    PRINT : PRINT org$
    PRINT : PRINT "This is one of the files 2wegraph most recently
        processed"
    PRINT "Do you want to access the information in this file?"
1880 a$ = INKEY$: IF a$ = "" THEN GOTO 1880 ELSE GOTO 1890
1890 IF a$ = "Y" OR a$ = "y" THEN GOTO 1900 ELSE GOTO 1860
1900 PRINT "Output format is:raw data, smoothed, last scan(smoothed),
        ratio, current, baseline data"
    PRINT org$
    PRINT nu
    PRINT sc$
    PRINT scl$
    PRINT rt$
    PRINT ip$
    PRINT "Are these the names of the files you wish to ascess? <y>?"
1901 a$ = INKEY$: IF a$ = "" THEN GOTO 1901
    IF a$ = "y" OR a$ = "Y" THEN GOTO 1903 ELSE GOTO 1902
1902 INPUT "Enter the name of the file which contains the Scans"; sc$
    INPUT "Enter the name of the file which contains the Last Scan"; scl$
    INPUT "Enter the name of the file which contains the Ratio info"; rt$
    INPUT "Enter the name of the file which contains the Ratio and Ipc
        info";ip$
    INPUT "Enter the number of scans contained in the original file"; nu
1903 IF cycles = 0 THEN DIM R%(nu, 2)
    cycles = 1
    CLOSE #1
    GOTO 90
    '
    ' ****Extrapolate a Baseline?
2002 CLS
    INPUT "input the number of the scan you wish to show";scannum
    scancnt = 1
    PRINT "Have you already extrapolated a baseline for this file and"
    PRINT "was this file one of the files listed in the beginning of the
        program?"
    PRINT "Hit <y> if both of the above conditions are true, else hit anykey to
        continue"
2010 a$ = INKEY$: IF a$ = "" GOTO 2010
    IF a$ = "y" OR a$ = "Y" THEN GOTO 2600
    OPEN "c:\mccme\data\" + sc$ FOR INPUT AS #3
2130 FOR i = 0 TO npts% - 21
    INPUT #3, fit(i, 0)
    IF EOF(3) THEN GOTO 2220 ELSE GOTO 2160
2160 INPUT #3, fit(i, 1)
```

```
    IF EOF(3) THEN GOTO 2220 ELSE GOTO 2180
2180 INPUT #3, fit(i, 2)
    IF EOF(3) THEN GOTO 2220 ELSE GOTO 2200
2200 NEXT i
2220 CLOSE #3
    CLS : SCREEN 2
    y = 0
    z = 100
1830 sumx = 0
    sumx2 = 0
    sumy = 0
    sumy2 = 0
    sumxy = 0
    FOR i = y TO z
    sumx = sumx + fit(i, 0)
    sqrx = (fit(i, 0) ^ 2)
    sumx2 = sumx2 + sqrx
    sumy = sumy + fit(i, 1)
    sqry = (fit(i, 1) ^ 2)
    sumy2 = sumy2 + sqry
    sumxy = sumxy + (fit(i, 0) * fit(i, 1))
    NEXT i
    div2 = INT(z - y)
    xmean = (sumx / div2)
    ymean = (sumy / div2)
    a2 = (sumx2 - ((sumx ^ 2) / div2))
    b2 = (sumy2 - ((sumy ^ 2) / div2))
    AB = (sumxy - ((sumx * sumy) / div2))
    cmeslope = AB / a2
    cmeyint = ymean - (cmeslope * xmean)
    '
    X = YINT + ((fit(y, 0) * SLOPE) * -1)
    Y1 = (100 - ((fit(y, 1) * CONV2 * 10) * QCONV2 * scale))
    PSET (X, Y1)
    FOR i = 0 TO half
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
    Y1 = (100 - ((fit(i, 1) * CONV2 * 10) * QCONV2 * scale))
    LINE -(X, Y1)
    NEXT i
    '
    bline = (cmeslope * fit(y, 0)) + cmeyint
    X = YINT + ((fit(y, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2 * scale))
    PSET (X, Y1)
```

```
    FOR i = 0 TO half
    bline = (cmeslope * fit(i, 0)) + cmeyint
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2 * scale))
    LINE -(X, Y1)
    NEXT i
    '
    LOCATE 5, 5
    PRINT "This is the extrapolated baseline for the CME, is it acceptable?"
1930 a$ = INKEY$: IF a$ = "" GOTO 1930
    IF a$ = "y" OR a$ = "Y" THEN GOTO 2000 ELSE GOTO 1950
1950 PRINT "The current length of the baseline is"; y;
        "to"; z
    INPUT "Enter the new starting point for the baseline"; y$
    INPUT "Enter the new stopping point for the baseline"; z$
    y = VAL(y$): z = VAL(z$)
    CLS : GOTO 1830
    '
2000 w = y: V = z
    CLS
2020 sumx = 0
    sumx2 = 0
    sumy = 0
    sumy2 = 0
    sumxy = 0
    FOR i = w TO V
    sumx = sumx + fit(i, 0)
    sqrx = (fit(i, 0) ^ 2)
    sumx2 = sumx2 + sqrx
    sumy = sumy + fit(i, 2)
    sqry = (fit(i, 2) ^ 2)
    sumy2 = sumy2 + sqry
    sumxy = sumxy + (fit(i, 0) * fit(i, 2))
    NEXT i
    div2 = INT(V - w)
    xmean = (sumx / div2)
    ymean = (sumy / div2)
    a2 = (sumx2 - ((sumx ^ 2) / div2))
    b2 = (sumy2 - ((sumy ^ 2) / div2))
    AB = (sumxy - ((sumx * sumy) / div2))
    bareslope = AB / a2
    bareyint = ymean - (bareslope * xmean)
    '
    X = YINT + ((fit(w, 0) * SLOPE) * -1)
```

```
    y2 = (100 - ((fit(w, 2) * CONV2 * 10) * QCONV * scale))
    PSET (X, y2)
    FOR i = 0 TO half
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
    y2 = (100 - ((fit(i, 2) * CONV2 * 10) * QCONV * scale))
    LINE -(X, y2)
    NEXT i
    '
    bline = (bareslope * fit(w, 0)) + bareyint
    X = YINT + ((fit(w, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2 * scale))
    PSET (X, Y1)
    FOR i = 0 TO half
    bline = (bareslope * fit(i, 0)) + bareyint
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2 * scale))
    LINE -(X, Y1)
    NEXT i
    '
    LOCATE 5, 5
    PRINT "This is the extrapolated baseline for the bare electrode, is it
        acceptable?"
2120 a$ = INKEY$: IF a$ = "" GOTO 2120 ELSE GOTO 2125
2125 IF a$ = "y" OR a$ = "Y" THEN GOTO 2190 ELSE GOTO 2140
2140 PRINT "The current length of the baseline is"; w;"to"; V
    INPUT "Enter the new starting point for the baseline"; w$
    INPUT "Enter the new stopping point for the baseline"; V$
    w = VAL(w$): V = VAL(V$)
    CLS : GOTO 2020
    '
2190 CLS
    q = 0: R = 100
2210 q2 = q + half: r2 = R + half
    sumx = 0
    sumx2 = 0
    sumy = 0
    sumy2 = 0
    sumxy = 0
    FOR i = q2 TO r2
    sumx = sumx + fit(i, 0)
    sqrx = (fit(i, 0) ^ 2)
    sumx2 = sumx2 + sqrx
    sumy = sumy + fit(i, 1)
    sqry = (fit(i, 1) ^ 2)
```

```
    sumy2 = sumy2 + sqry
    sumxy = sumxy + (fit(i, 0) * fit(i, 1))
    NEXT i
    div2 = INT(r2 - q2)
    xmean = (sumx / div2)
    ymean = (sumy / div2)
    a2 = (sumx2 - ((sumx ^ 2) / div2))
    b2 = (sumy2 - ((sumy ^ 2) / div2))
    AB = (sumxy - ((sumx * sumy) / div2))
    cmeslope2 = AB / a2
    cmeyint2 = ymean - (cmeslope2 * xmean)
    '
    X = YINT + ((fit(q2, 0) * SLOPE) * -1)
    Y1 = (100 - ((fit(q2, 1) * CONV2 * 10) * QCONV2 * scale))
    PSET (X, Y1)
    FOR i = half TO npts% - 21
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
    Y1 = (100 - ((fit(i, 1) * CONV2 * 10) * QCONV2 * scale))
    LINE -(X, Y1)
    NEXT i
    '
    bline = (cmeslope2 * fit(q2, 0)) + cmeyint2
    X = YINT + ((fit(q2, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2 * scale))
    PSET (X, Y1)
    FOR i = half TO npts% - 21
    bline = (cmeslope2 * fit(i, 0)) + cmeyint2
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2 * scale))
    LINE -(X, Y1)
    NEXT i
    '
    LOCATE 5, 5
    PRINT "This is the extrapolated return baseline for the CME, is it
        acceptable?"
2320 a$ = INKEY$: IF a$ = "" GOTO 2320 ELSE GOTO 2330
2330 IF a$ = "y" OR a$ = "Y" THEN GOTO 2390 ELSE GOTO 2340
2340 PRINT "The current length of the baseline is"; q;
        "to"; R
2342 INPUT "Enter the new starting point for the baseline"; q$
    q = VAL(q$)
    IF q > 350 THEN
    PRINT "Value too large-Select smaller": GOTO 2342
    ELSEIF q < = 350 THEN GOTO 2343
```

```
    END IF
2343 INPUT "Enter the new stopping point for the baseline"; R$
    R = VAL(R$)
    IF R > 350 THEN
    PRINT "Value too large-Select smaller": GOTO 2343
    ELSEIF R <= 350 THEN GOTO 2344
    END IF
2344 CLS : GOTO 2210
    '
2390 CLS
    s = q: t = R
2410 s2 = s + half: t2 = t + half
    sumx = 0
    sumx2 = 0
    sumy = 0
    sumy2 = 0
    sumxy = 0
    FOR i = s2 TO t2
    sumx = sumx + fit(i, 0)
    sqrx = (fit(i, 0) ^ 2)
    sumx2 = sumx2 + sqrx
    sumy = sumy + fit(i, 2)
    sqry = (fit(i, 2) ^ 2)
    sumy2 = sumy2 + sqry
    sumxy = sumxy + (fit(i, 0) * fit(i, 2))
    NEXT i
    div2 = INT(t - s)
    xmean = (sumx / div2)
    ymean = (sumy / div2)
    a2 = (sumx2 - ((sumx ^ 2) / div2))
    b2 = (sumy2 - ((sumy ^ 2) / div2))
    AB = (sumxy - ((sumx * sumy) / div2))
    bareslope2 = AB / a2
    bareyint2 = ymean - (bareslope2 * xmean)
    '
    X = YINT + ((fit(s2, 0) * SLOPE) * -1)
    y2 = (100 - ((fit(s2, 2) * CONV2 * 10) * QCONV * scale))
    PSET (X, y2)
    FOR i = half TO npts% - 21
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
    y2 = (100 - ((fit(i, 2) * CONV2 * 10) * QCONV * scale))
    LINE -(X, y2)
    NEXT i
    '
```

```
    bline = (bareslope2 * fit(s2, 0)) + bareyint2
    X = YINT + ((fit(s2, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2 * scale))
    PSET (X, Y1)
    FOR i = half TO npts% - 21
    bline = (bareslope2 * fit(i, 0)) + bareyint2
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2 * scale))
    LINE -(X, Y1)
    NEXT i
    '
    LOCATE 5, 5
    PRINT "This is the extrapolated return baseline for the bare electrode,
        is it acceptable?"
2520 a$ = INKEY$: IF a$ = "" GOTO 2520
    IF a$ = "y" OR a$ = "Y" THEN GOTO 2600 ELSE GOTO 2540
2540 PRINT "The current length of the baseline is"; s; "to"; t
2542 INPUT "Enter the new starting point for the baseline"; s$
    s = VAL(s$)
    IF s > 350 THEN
    PRINT "Value too large-Select smaller": GOTO 2542
    ELSEIF s <= 350 THEN GOTO 2543
    END IF
2543 INPUT "Enter the new stopping point for the baseline"; t$
    t = VAL(t$)
    IF t > 350 THEN
    PRINT "Value too large-Select smaller": GOTO 2543
    ELSEIF t <= 350 THEN GOTO 2544
    END IF
2544 CLS : GOTO 2410
    '
2600 CLS
    PRINT "Choose an option:"
    PRINT "1. Print out the final scan for the CME"
    PRINT "2. Print out the final scan for the bare electrode"
    PRINT "3. Print out both final scans on the same screen"
2610 z$ = INKEY$: IF z$ = "" THEN GOTO 2610 ELSE GOTO 2620
2620 z = VAL(z$)
    INPUT "Input the concentration of the solution used (or other info)"; conc$
    '
    CLS : SCREEN 2
    LOCATE 20, 2
    PRINT vs
    i = 1
```

```
    FOR j = (vs - XSTP) TO vsw STEP -XSTP
    LOCATE 20, 74 / 10 * (i)
    PRINT USING "#.#"; j
    i = i + 1
    NEXT j
    LOCATE 20, 74
    PRINT vsw
    '
    IF z = 1 OR z = 3 THEN GOTO 2630 ELSE GOTO 2680
2630 OPEN "c:\mccme\data\" + sc$ FOR INPUT AS #3
2631 FOR i = 0 TO npts% - 21
    INPUT #3, fit(i, 0), fit(i, 1), fit(i, 2)
    NEXT i
    scancnt = scancnt + 1
    IF scancnt = scannum THEN GOTO 2670 ELSE GOTO 2631
    '
2670 IF z = 2 OR z = 3 THEN CLOSE #3
    X = YINT + ((fit(0, 0) * SLOPE) * -1)
    Y1 = (100 - ((fit(0, 1) * CONV2 * 10) * QCONV2 * scale))
    PSET (X, Y1)
    FOR i = 0 TO npts% - 21
    x2 = YINT + ((fit(i, 0) * SLOPE) * -1)
    y2 = (100 - ((fit(i, 1) * CONV2 * 10) * QCONV * scale))
    LINE -(x2, y2)
    NEXT i
    '
    bline = (cmeslope * fit(0, 0)) + cmeyint
    X = YINT + ((fit(0, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2 * scale))
    PSET (X, Y1)
    FOR i = 0 TO half
    bline = (cmeslope * fit(i, 0)) + cmeyint
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2 * scale))
    LINE -(X, Y1)
    NEXT i
    '
    bline = (cmeslope2 * fit(half, 0)) + cmeyint2
    X = YINT + ((fit(half, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2 * scale))
    PSET (X, Y1)
    FOR i = half TO npts% - 21
    bline = (cmeslope2 * fit(i, 0)) + cmeyint2
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
```

```
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2 * scale))
    LINE -(X, Y1)
    NEXT i
    '
2680 IF z = 2 OR z = 3 THEN GOTO 2690 ELSE GOTO 2730
2690 OPEN "c:\mccme\data\" + sc$ FOR INPUT AS #3
2691 FOR i = 0 TO npts% - 21
    INPUT #3, fit(i, 0), fit(i, 1), fit(i, 2)
       NEXT i
    scancnt = scancnt + 1
    IF scancnt >= scannum THEN GOTO 2695 ELSE GOTO 2691
    '
2695 X = YINT + ((fit(0, 0) * SLOPE) * -1)
    Y1 = (100 - ((fit(0, 2) * CONV2 * 10) * QCONV2 * scale))
    PSET (X, Y1)
    FOR i = 0 TO npts% - 21
    x2 = YINT + ((fit(i, 0) * SLOPE) * -1)
    y2 = (100 - ((fit(i, 2) * CONV2 * 10) * QCONV * scale))
    LINE -(x2, y2)
    NEXT i
    '
    bline = (bareslope * fit(0, 0)) + bareyint
    X = YINT + ((fit(0, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2 * scale))
    PSET (X, Y1)
    FOR i = 0 TO half
    bline = (bareslope * fit(i, 0)) + bareyint
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2 * scale))
    LINE -(X, Y1)
    NEXT i
    '
    bline = (bareslope2 * fit(half, 0)) + bareyint2
    X = YINT + ((fit(half, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2 * scale))
    PSET (X, Y1)
    FOR i = half TO npts% - 21
    bline = (bareslope2 * fit(i, 0)) + bareyint2
    X = YINT + ((fit(i, 0) * SLOPE) * -1)
    Y1 = (100 - ((bline * CONV2 * 10) * QCONV2 * scale))
    LINE -(X, Y1)
    NEXT i
    '
2730 LOCATE 2, 1
```

```
    PRINT "Hit print screen to print"
    LOCATE 3, 1
    PRINT "type <exit> when done"
    LOCATE 4, 2
    IF z = 1 THEN PRINT "CME"
    IF z = 2 THEN PRINT "BARE"
    IF z = 3 THEN PRINT "CME + BARE"
    LOCATE 5, 2
    PRINT conc$
    LOCATE 21, 5
    SHELL
    PRINT "Do you want to show the next scan as well?"
2731 a$ = INKEY$: IF a$ = "" THEN GOTO 2731
    IF a$ = "y" OR a$ = "Y" THEN GOTO 2732 ELSE GOTO 2733
2732 CLS
    INPUT "Do you have any new info to print?"; conc$
    LOCATE 20, 2
    PRINT vs
    i = 1
    FOR j = (vs - XSTP) TO vsw STEP -XSTP
    LOCATE 20, 74 / 10 * (i)
    PRINT USING "#.#"; j
    i = i + 1
    NEXT j
    LOCATE 20, 74
    PRINT vsw
    GOTO 2691
2733 CLOSE #3
    GOTO 90
    '
    '***Routine to print out the final scan
    '
3450 CLS
    PRINT "Choose an option:"
    PRINT "1. Print out the final scan for the CME"
    PRINT "2. Print out the final scan for the bare electrode"
    PRINT "3. Print out both final scans on the same screen"
    PRINT "4. Change the scaling on the graph"
3510 z$ = INKEY$: IF z$ = "" THEN GOTO 3510 ELSE GOTO 3520
3520 z = VAL(z$)
    IF z = 4 GOTO 3525 ELSE GOTO 3527
3525 INPUT "Input the new scaling factor for the graph"; scale
    GOTO 3450
3527 INPUT "Input the concentration of the solution used (or other info)"; conc$
```

```
    CLS : SCREEN 2
    LOCATE 20, 2
    PRINT vs
    i = 1
    FOR j = (vs - XSTP) TO vsw STEP -XSTP
    LOCATE 20, 74 / 10 * (i)
    PRINT USING "#.#"; j
    i = i + 1
    NEXT j
    LOCATE 20, 74
    PRINT vsw
    IF z = 1 OR z = 3 THEN GOTO 3660 ELSE GOTO 3820
3660 OPEN "c:\mccme\data\" + scl$ FOR INPUT AS #3
    FOR i = 0 TO npts% - 21
    INPUT #3, fit(i, 0)
    x2 = YINT + ((fit(i, 0) * SLOPE) * -1)
    IF EOF(3) THEN GOTO 3810 ELSE GOTO 3710
3710 INPUT #3, fit(i, 1)
    y2 = (100 - ((fit(i, 1) * CONV2 * 10) * QCONV2 * scale))
    IF EOF(3) THEN GOTO 3810 ELSE GOTO 3750
3750 INPUT #3, fit(i, 2)
    IF EOF(3) THEN GOTO 3810 ELSE GOTO 3770
3770 LINE -(x2, y2)
    NUMRUN = 1
    NEXT i
3810 CLOSE #3
3820 IF z = 2 OR z = 3 THEN GOTO 3830 ELSE GOTO 3990
3830 OPEN "c:\mccme\data\" + scl$ FOR INPUT AS #3
    FOR i = 0 TO npts% - 21
    INPUT #3, fit(i, 0)
    x2 = YINT + ((fit(i, 0) * SLOPE) * -1)
    IF EOF(3) THEN GOTO 3990 ELSE GOTO 3890
3890 INPUT #3, fit(i, 1)
    IF EOF(3) THEN GOTO 3990 ELSE GOTO 3910
3910 INPUT #3, fit(i, 2)
    y2 = (100 - ((fit(i, 2) * CONV2 * 10) * QCONV * scale))
    IF EOF(3) THEN GOTO 3990 ELSE GOTO 3950
3950 LINE -(x2, y2)
    NEXT i
3990 CLOSE #3
    LOCATE 2, 1
    PRINT "Hit print screen to print"
    LOCATE 3, 1
    PRINT "type <exit> when done"
```

```
    LOCATE 4, 2
    IF z = 1 THEN PRINT "CME"
    IF z = 2 THEN PRINT "BARE"
    IF z = 3 THEN PRINT "CME + BARE"
    LOCATE 5, 2
    PRINT conc$
    LOCATE 21, 5
    SHELL
    GOTO 90
4130 '
    '***Routine to print out every Xth scan
    '
    CLS
    PRINT "Choose an option:"
    PRINT "1. Print out scans for the CME"
    PRINT "2. Print out scans for the bare electrode"
    PRINT "3. Change the scaling for the graph"
4200 z$ = INKEY$: IF z$ = "" THEN GOTO 4200 ELSE GOTO 4210
4210 z = VAL(z$)
    IF z = 3 THEN GOTO 4212 ELSE GOTO 4213
4212 INPUT "Input the new scaling factor for the graph"; scale
    GOTO 4130
4213 INPUT "Input every Xth Scan which you want graphed"; xth
    INPUT "Input the concentration of the test solution (or other info)"; conc$
    OPEN "c:\mccme\data\" + sc$ FOR INPUT AS #3
    CLS : SCREEN 2
    NUMRUN = 1
    LOCATE 20, 2
    PRINT vs
    i = 1
    FOR j = (vs - XSTP) TO vsw STEP -XSTP
    LOCATE 20, 74 / 10 * (i)
    PRINT USING "#.#"; j
    i = i + 1
    NEXT j
    LOCATE 20, 74
    PRINT vsw
4370 FOR i = 0 TO npts% - 21
    INPUT #3, fit(i, 0)
    x2 = YINT + ((fit(i, 0) * SLOPE) * -1)
    IF EOF(3) THEN GOTO 4620 ELSE GOTO 4450
4450 INPUT #3, fit(i, 1)
    y2 = (100 - ((fit(i, 1) * CONV2 * 10) * QCONV2 * scale))
    IF EOF(3) THEN GOTO 4620 ELSE GOTO 4500
```

```
4500 INPUT #3, fit(i, 2)
    Y3 = (100 - ((fit(i, 2) * CONV2 * 10) * QCONV * scale))
    IF EOF(3) THEN GOTO 4620 ELSE GOTO 4550
4550 IF NUMRUN = xth THEN GOTO 4570 ELSE GOTO 4580
4570 IF z = 1 THEN LINE -(x2, y2) ELSE LINE -(x2, Y3)
    LOCATE 2, 1
    PRINT "Hit print screen to print"
    LOCATE 3, 1
    PRINT "type <exit> when done"
    LOCATE 4, 1
    IF z = 1 THEN PRINT "CME" ELSE PRINT "BARE"
    LOCATE 5, 1
    PRINT conc$
    LOCATE 21, 5
    SHELL
4580 NEXT i
    IF NUMRUN = xth THEN NUMRUN = 0 ELSE NUMRUN = NUMRUN + 1
    GOTO 4370
4620 CLOSE #3
    GOTO 90
    '
    '
    '***Routine to print out all scans
    '
4780 CLS
    PRINT "Choose an option:"
    PRINT "1. Print out all scans for the CME"
    PRINT "2. Print out all scans for the bare electrode"
    PRINT "3. Change the scaling for the graph"
4820 z$ = INKEY$: IF z$ = "" THEN GOTO 4820 ELSE GOTO 4830
4830 z = VAL(z$)
    IF z = 3 THEN GOTO 4831 ELSE GOTO 4832
4831 INPUT "Input the new scaling factor for the graph"; scale
    GOTO 4780
4832 INPUT "Input the concentration of the test solution (or other info)"; conc$
    OPEN "c:\mccme\data\" + sc$ FOR INPUT AS #3
    CLS : SCREEN 2
    LOCATE 20, 2
    PRINT vs
    i = 1
    FOR j = (vs - XSTP) TO vsw STEP -XSTP
    LOCATE 20, 74 / 10 * (i)
    PRINT USING "#.#"; j
    i = i + 1
```

```
    NEXT j
    LOCATE 20, 74
    PRINT vsw
4980 FOR i = 0 TO npts% - 21
    INPUT #3, fit(i, 0)
    x2 = YINT + ((fit(i, 0) * SLOPE) * -1)
    IF EOF(3) THEN GOTO 5170 ELSE GOTO 5020
5020 INPUT #3, fit(i, 1)
    y2 = (100 - ((fit(i, 1) * CONV2 * 10) * QCONV2 * scale))
    IF EOF(3) THEN GOTO 5170 ELSE GOTO 5070
5070 INPUT #3, fit(i, 2)
    Y3 = (100 - ((fit(i, 2) * CONV2 * 10) * QCONV * scale))
5110 IF EOF(3) THEN GOTO 5170 ELSE GOTO 5120
5120 IF z = 1 THEN LINE -(x2, y2) ELSE LINE -(x2, Y3)
    NEXT i
    GOTO 4980
5170 CLOSE #3
    LOCATE 2, 1
    PRINT "Hit print screen to print"
    LOCATE 3, 1
    PRINT "type <exit> when done"
    LOCATE 4, 1
    IF z = 1 THEN PRINT "CME" ELSE PRINT "BARE"
    LOCATE 5, 1
    PRINT conc$
    LOCATE 21, 5
    SHELL
    GOTO 90
    '
    '****Routine to print out Ratio vs Time
5310 OPEN "c:\mccme\data\" + rt$ FOR INPUT AS #1
    INPUT "Input the expected maximum ratio"; rmax
    INPUT "input the expected number of scans"; smax
    CLS : SCREEN 2: KEY OFF
    LOCATE 3, 10
    PRINT "Hit print screen to print"
    LOCATE 4, 10
    PRINT "type <exit> when done"
    LOCATE 23, 1
    PRINT "0.0"
    TINT% = INT(smax / 10)
    j = 1
    FOR i = TINT% TO (smax - TINT%) STEP TINT%
    place = INT(j * (8))
```

```
    IF place > 72 THEN GOTO 5320
    LOCATE 23, place
    PRINT USING "##.#"; i
5320 j = j + 1
    NEXT i
    RINT = (rmax / 10)
    RINT2 = RINT
    FOR i = 21 TO 2 STEP -2
    LOCATE i, 1
    PRINT USING "##.#"; RINT2
    RINT2 = RINT2 + RINT
    NEXT i
       INPUT #1, R%(1, 0), R%(1, 1)
    X1 = (R%(1, 0) * 576 / smax) + 8
    Y1 = (180 - (160 * (R%(1, 1) / rmax)))
    PSET (X1, Y1)
    FOR i = 0 TO nu
    INPUT #1, R%(i, 0), R%(i, 1)
    X1 = (R%(1, 0) * 576 / smax) + 8
    Y1 = (184 - (160 * (R%(1, 1) / rmax)))
    LINE -(X1, Y1)
    IF EOF(1) THEN GOTO 5650
    NEXT i
5650 CLOSE #1
    LOCATE 22, 1
    SHELL
    GOTO 90
    '
    ' Routine to print out the Ratio, Ipc Info
    '
5720 WIDTH LPRINT 80
    INPUT "Input the name of the original file, if desired"; flname$
    INPUT "Input relavent info for the file, if desired"; info$
    LPRINT flname$
    LPRINT info$
    PRINT "Choose an option:"
    PRINT "1. Print out the information for all scans"
    PRINT "2. Print out the information for every Xth scans"
    PRINT "3. Print out the information for the last scan"
    PRINT "4. Print out the ratio for the first x scans"
    PRINT "5. Print out the ratio from scan X to scan Z"
5760 z$ = INKEY$: IF z$ = "" THEN GOTO 5760 ELSE GOTO 5770
5770 z = VAL(z$)
    ON z GOTO 5790, 5870, 5990, 6000, 7000
```

```
5790 OPEN "c:\mccme\data\" + ip$ FOR INPUT AS #2
5800 IF EOF(2) THEN GOTO 5850
    LINE INPUT #2, L$
    IF EOF(2) THEN GOTO 5850
    LINE INPUT #2, ls$
    IF EOF(2) THEN GOTO 5850
    LINE INPUT #2, lz$
    PRINT L$
    PRINT ls$
    PRINT lz$
    LPRINT L$
    LPRINT ls$
    LPRINT lz$
    LPRINT ""
    GOTO 5800
5850 CLOSE #2: GOTO 90
    '
5870 INPUT "Input the number of the Xth scan for which you wish to print out
        the information"; xth
    NUMRUN = 1
    OPEN "c:\mccme\data\" + ip$ FOR INPUT AS #2
5900 IF EOF(2) THEN GOTO 5970
    LINE INPUT #2, L$
    LINE INPUT #2, ls$
    LINE INPUT #2, lz$
    IF NUMRUN = xth THEN GOTO 5930 ELSE GOTO 5950
5930 PRINT L$
    PRINT ls$
    PRINT lz$
    LPRINT L$
    LPRINT ls$
    LPRINT lz$
    LPRINT ""
5950 IF NUMRUN = xth THEN NUMRUN = 1 ELSE NUMRUN =
        NUMRUN + 1
    GOTO 5900
5970 CLOSE #2: GOTO 90
    '
5990 OPEN "c:\mccme\data\" + ip$ FOR INPUT AS #2
    NUMRUN = 1
6010 IF EOF(2) THEN GOTO 6080
    LINE INPUT #2, L$
    LINE INPUT #2, ls$
    LINE INPUT #2, lz$
```

```
    IF EOF(2) THEN GOTO 6040 ELSE GOTO 6060
6040 PRINT L$
    PRINT ls$
    PRINT lz$
    LPRINT L$
    LPRINT ls$
    LPRINT lz$
    LPRINT ""
6060 NUMRUN = NUMRUN + 1
    GOTO 6010
6080 CLOSE #2: GOTO 90
    '
6000 INPUT "Input the Xth number of scans for which you wish to print out
        the information"; xth
    NUMRUN = 0
    OPEN "c:\mccme\data\" + ip$ FOR INPUT AS #2
6200 IF EOF(2) THEN GOTO 6220
    LINE INPUT #2, L$
    LINE INPUT #2, ls$
    LINE INPUT #2, lz$
    PRINT L$
    PRINT ls$
    PRINT lz$
    LPRINT L$
    LPRINT ls$
    LPRINT lz$
    LPRINT ""
    NUMRUN = NUMRUN + 1
    IF NUMRUN = xth THEN GOTO 6220 ELSE GOTO 6200
6220 CLOSE #2: GOTO 90
    '
7000 INPUT "Input the number of the Xth scan for which you wish to begin to
        print out data"; xth
    INPUT "Input the number of the Zth scan for which you wish to stop data
        printout"; zTH
    NUMRUN = -1
    OPEN "c:\mccme\data\" + ip$ FOR INPUT AS #2
7010 NUMRUN = NUMRUN + 1
    IF EOF(2) THEN GOTO 7030
    LINE INPUT #2, L$
    IF EOF(2) THEN GOTO 7030
    LINE INPUT #2, ls$
    IF EOF(2) THEN GOTO 7030
    LINE INPUT #2, lz$
```

```
    '
    PRINT NUMRUN
    IF NUMRUN >= xth THEN GOTO 7020 ELSE GOTO 7025
7020 PRINT L$
    PRINT ls$
    PRINT lz$
    LPRINT L$
    LPRINT ls$
    LPRINT lz$
    LPRINT ""
7025 IF NUMRUN >= zTH THEN GOTO 7030 ELSE GOTO 7010
7030 CLOSE #2: GOTO 90
    '
6100 END
```

APPENDIX 2

PUBLISHED ARTICLE

ON

WORK NOT PRESENTED IN DISSERTATION

Electroanalysis, 6(1994) 23-28

Dual Wall-Tube Electrode Cell for Use in Clay-Modified Electrode Studies

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ABSTRACT

A dual tube-electrode cell has been constructed for use in clay-modified electrode (CME) studies. The optimization and characterization of the wall-tube cell through both visual and electrochemical measurements is described. Its use in some CME studies is then described. The system is found to give excellent insight into the behavior of a CME.

KEY WORDS: Modified electrodes, Clays, Wall-Tube cell.

INTRODUCTION

In this article, the construction and use of a wall-tube electrode with two working electrodes are described. The dual wall-tube electrode cell contains a clay-modified working electrode and an unmodified platinum working electrode in addition to the usual counter and reference electrodes. The setup is comparable to that of a dual beam spectrophotometer in that it has a reference and a sample cell. To the best of our knowledge, this is the first report of this type of dual electrode cell.

We chose to work with the wall-tube electrode because of the well-defined nature of the system [1]. The wall-tube has a small effective cell volume and, hence, gives a rapid switching time for electrolytes. When the jet impinges upon the electrode, it creates a region of flow made up entirely of flow from the jet [2]. This area is termed the hydrodynamic boundary layer and constitutes the cell volume which the electrode samples [3]. Since in the wall-tube electrode the radius of the jet is much larger then that of the electrode, the electrode area is uniformly accessible to the impinging solution [2]. By combining these features with the control over the electrochemical diffusion layer obtained with cyclic voltammetry, good control was achieved over the processes which occurred in the system.

We have studied clay modified electrodes (CMEs) as a means of understanding the diffusional properties of the clay. Recent work in our laboratory has demonstrated a correlation between the ratio of the maximum reduction currents obtained at the CME (I_{pcme}) and the maximum reduction current obtained at the bare electrode (I_{pbare}) for $Fe(CN)_6^{3-}$ ($R = I_{pcme}/I_{pbare}$) and low-angle X-ray diffraction data [4]. Based on these data, a correlation between reduction currents for $Fe(CN)_6^{3-}$ at CMEs and the interlayer spacing within the clay film is suggested [5]. Knowledge of the interlayer spacing is an important first step in understanding the diffusional properties of clay films. In this work, we hope to use this knowledge to gain an understanding of the clay beds which underlie waste disposal sites throughout the country.

The dual wall-tube electrode was constructed for use in the clay ratio studies. Using a flow system enabled us to make a set of experimental measurements on a single clay film. In previous studies, it was necessary to create a new CME for each measurement. When the electrode was switched between different electrolyte concentrations, the clay film was exposed to the atmosphere which may lead to drying. When a swollen clay film is dried, it may form structures which are impervious to change [6]. In the wall-tube system, we were able to keep the clay film hydrated throughout the duration of the experiment, thus eliminating the necessity of making a new electrode for each measurement. This, along with the incorporation of the CME and the bare electrode into the same system cut the time for an experiment substantially. In addition, the use of the dual wall-tube system mitigated any errors which were due to improper matching of experimental parameters. Thus, we were able to eliminate the error introduced by the variability inherent in using different clay films for a set of measurements, cut the time for an experimental run substantially, and reduce experimental error through the use of the dual wall-tube electrode.

MATERIALS AND METHODS

$K_3Fe(CN)_6$, NaCl, acetone, methanol, and ethanol (Aldrich, Milwaukee, WI) and food coloring (McCormick Brand, Baltimore, MD) were used as received. SWY-1

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1040-0397/94/$5.00 + .25

montmorillonite was obtained from the source repository (Department of Geology, University of Missouri, Columbia) and prepared as previously described [4]. All solutions were purged with N_2 prior to measurements.

Electrodes were constructed in-house from 0.040 in. diameter Pt wire (D.F. Goldsmith, Evanston, IL) sealed in 0.750 in. diameter soft glass. Electrical connections were made with a copper pin joint soldered to copper wire. Electrode areas were calculated from the diffusion controlled peaks of $Fe(CN)_6^{3-}$. Electrodes labeled S_1 and S_2 were used in the sample position and as CMEs. Their areas were calculated respectively as 7.49 ± 1.31 and 7.47 ± 1.06 × 10^{-3} cm^2. Electrode S_2 was used in the irreversible swelling studies, while electrode S_1 was used in all other work. Electrode R was used as the electrode for the reference jet in all experiments. Its area was calculated to be 7.47 ± 1.11 × 10^{-3} cm^2.

Electrodes were polished on a Buelher polishing wheel with a Buelher microcloth and with 0.05 μm alumina using copious amounts of water. The electrodes were then rinsed and sonicated to remove any remaining Al_2O_3. This procedure was performed prior to addition of clay for the CME and prior to the beginning of any run for the bare electrode.

Oven dried clay-modified electrodes (ODCMEs) were prepared by drying 1 μL of a 10 g l^{-1} stock solution on the Pt surface rapidly for 10 minutes at 100°C followed by 5 minutes of cooling and air drying. Spin coated clay-modified electrodes (SPCMEs) were prepared by applying 1 μL of a 35 g l^{-1} stock solution to the electrode. The electrode was inserted into an inverted Pine MSR electrode rotator and spun at 800 rpm for 15 minutes.

An EGG PAR 175 universal programmer coupled with a EGG PAR 173 potentiostat were used for all measurements. The CME current was run through the potentiostat and recorded on a PAR RE 00091 X-Y recorder. The bare electrode current was run through a current-to-voltage converter (constructed in-house) and recorded on a PAR RE 00074 X-Y recorder. All scans were performed at +0.8 to −0.2 V versus a SCE at a 500 mV/s scan rate. A platinum counter electrode was used.

A wall-tube electrode compartment was constructed from a machined solid Teflon (Interplast, Burlington, NJ) block coupled with 1/8 in. Plexiglass. Internal dimensions of the cell were 6 × 4.8 × 1.9 cm. Universal Teflon adapters (Kontes, Vineland, MD) were used to ensure reproducible electrode positioning and a leak-proof seal. The jet was constructed from a 3/32 in. i.d. glass piece attached to the end of Tygon R-3603 3/32 in. i.d. tubing. A Rainin Rabbit model peristaltic pump was used for liquid flow. The two flow streams were split via a polyethylene y-joint (Aldrich) prior to the pump. A diagram of the entire setup is shown in Figure 1.

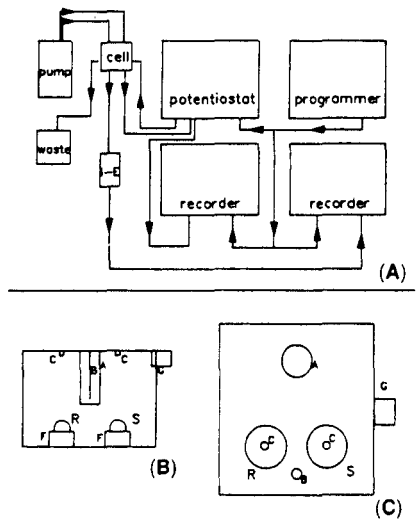

FIGURE 1. (A) Schematic of setup used in experiments. (B) Side view of wall-tube cell. (C) Top view of wall-tube cell. (A) reference electrode; (B) counter electrode; (C) jets; (S) CME working electrode: the sample position in all experiments; (R) bare working electrode: the "reference" position in all experiments; (F) electrode positioners; and (G) waste outlet.

Time of Swelling Studies

The CME and the bare electrode were placed in the wall-tube cell, and the cell was manually filled with approximately 35 mL of 1 M NaCl. The electrodes were equilibrated by scanning between the two potentials for 5 minutes in this solution. After this period, the pump was started and the electrolyte was introduced onto the electrode at a flow rate of 15 mL min^{-1} for the desired period of time. The solution was then switched to 1 M NaCl + 2 mM $Fe(CN)_6^{3-}$ at a flow rate of 5 mL min^{-1} by physically moving the tubing from one solution to the other and inserting an air bubble between the two solutions. The reduction current was measured until a steady state was achieved.

Swelling Studies

The electrodes were equilibrated, as previously described. After 5 minutes, the pump was started and 1 M NaCl was introduced onto the electrodes at 15 mL min^{-1} for a period of 8 minutes. The input solution was then switched to 1 M NaCl + 2 mM $Fe(CN)_6^{3-}$ at a flow rate of 5 mL min^{-1}. The current was measured until a steady state current was reached. The input solution was switched to the next lower concentration of electrolyte, and the process was repeated.

All kinematic viscosity data are either obtained directly from the CRC [7] or are calculated from density and viscosity data contained therein using the formula kinematic viscosity = viscosity (cP) / density (cS).

RESULTS AND DISCUSSION

Characterization of the Wall-Tube System

The wall-tube system used in this study differs from that of a classic wall-tube system in that it has two working electrodes. In order to use this system, the positioning

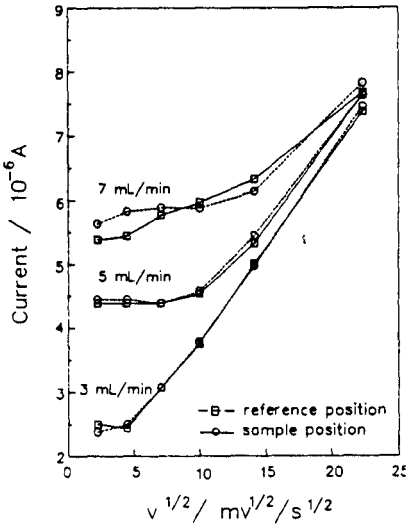

FIGURE 2. Plot of the cathodic peak height for 2 mM $Fe(CN)_6^{3-}$ in 1 M NaCl as a function of (scan rate)$^{1/2}$ for bare electrodes in the reference (-□-) (R in Figure 1) and sample (-O-) (S in Figure 1) positions of the wall-tube cell. Flow rates (in mL/min) are given above the sets of lines.

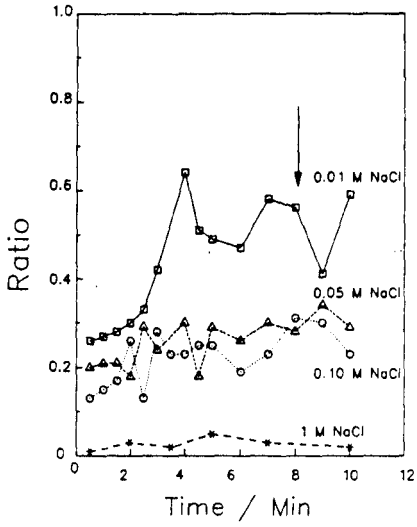

FIGURE 3. Plot of the ratio of the cathodic peak height (I_{pcme}/I_{pcbare}) for 2 mM $Fe(CN)_6^{3-}$ as a function of time of exposure to NaCl solution for a bare electrode (position R in Figure 1) and a 5 μg ODCME (position S in Figure 1). Concentrations of NaCl are given above the lines. The scan rate was 500 mV/s, and the Flow rate was 5 mL/min.

of the jet and the electrode had to be optimized, the electrodes and their positions matched, and there had to be no communication between the two positions. In addition, the behavior of the system had to be characterized.

The distance between the jet and the electrode effects the behavior of the wall-tube electrode [8]. In this system, the jet was inserted 0.7 mm into the cell and the electrode was inserted 8 mm into the cell. This resulted in a jet-electrode separation of 10.3 mm. At this separation, the system gave optimal performance.

A large volume cell was used to ensure no interference between the hydrodynamic boundary layers of the two electrodes. To verify that the jet flow onto the two electrodes did not interact, a visual study was made. The wall-tube cell was first filled with water. A colored solution was then run into the cell and the flow observed. Results visually show that the streams from the two jets and their resultant flows do not interfere with one another.

When the jet hits the electrode surface, it forms a boundary layer region. This layer is the effective cell volume for the system. The depth of the boundary layer can be calculated using Equation 1: [8].

$$\delta_{bl} = \upsilon^{1/2} r_j^{3/2} V_r^{-1/2} \qquad (1)$$

where υ is the kinematic viscosity of the solution, r_j is the radius of the jet, and V_r is the flow rate of the solution.

Using Equation 1, a maximum change in the depth in the boundary layer from 1.46×10^{-1} cm in 1 M NaCl to 1.43×10^{-1} cm in 0.01 M NaCl was calculated.

As a preliminary step in verifying the behavior of the system, the current was measured as a function of scan rate. When the electrochemical diffusion layer extends outside the boundary layer (fixed potential or slow potential scan rates), the current will be independent of scan rate and sigmoidal shaped CVs are observed. As the scan rate is increased, the diffusion layer moves within the boundary layer and scan rate dependent behavior is observed. Figure 2 shows the results of maximum (peak or plateau) current versus scan rate for a series of flow rates. The figure shows the close matching of the two electrode positions in their electrochemical response. Within the experimental parameters of this system, scan rates less than 200 mV/s resulted in scan rate independent currents. In order to use the wall-tube as a small sample cell holder, scan rates of 500 mV/s were used in subsequent work to ensure that the diffusion layer resided well within the clay film. From Figure 2, note that a scan rate of 500 mV/s results in linear diffusion at all flow rates, indicating that the diffusion layer resides within the hydrodynamic boundary layer.

Air Bubbles

Air bubbles are introduced between the input stream electrolyte solutions to prevent mixing of the two electrolyte solutions and, hence, a broadening of the solvent

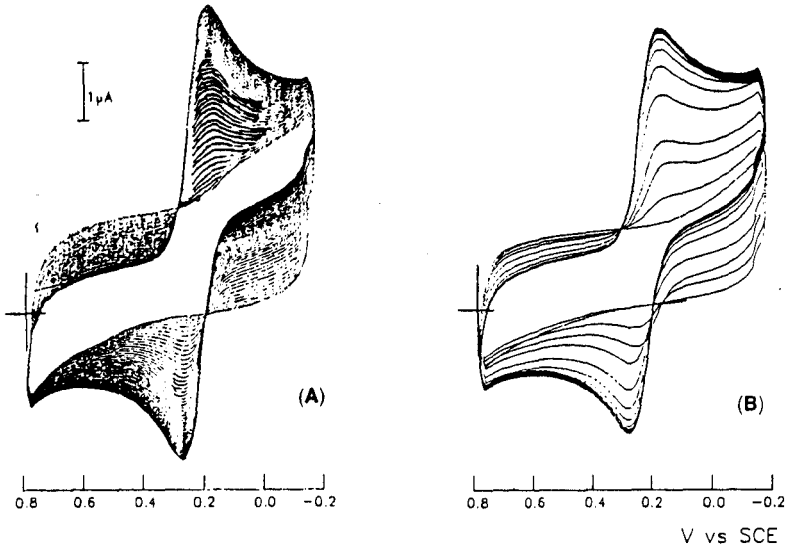

FIGURE 4. Multisweep cyclic voltammograms for (**A**) a 35 μg SPCME and (**B**) a 5 μg ODCME measured in 1 M NaCl + 2mM $Fe(CN)_6^{3-}$ after exposure to 0.03 M NaCl for 8 minutes. Arrows denote the direction of peak growth. The scan rate was 500 mV/s, and the flow rate was 5 mL/min.

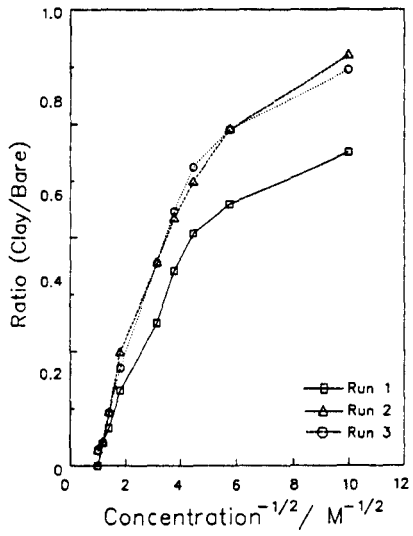

FIGURE 5. Plot of the ratio of the cathodic peak height for 2 mM $Fe(CN)_6^{3-}$ in 1 M NaCl at a bare electrode (position R in Figure 1) and a 5 μg ODCME (position S in Figure 1) after exposure to various concentrations of $[NaCl]^{-1/2}$ electrolyte solution for three different clay films. Time of exposure to the low concentration electrolyte solution was 8 minutes. The scan rate was 500 mV/s, and the flow rate was 5 mL/min.

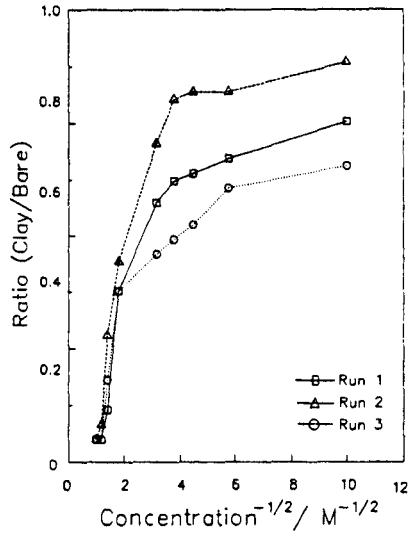

FIGURE 6. Plot of the ratio of the cathodic peak height for 2 mM $Fe(CN)_6^{3-}$ in 1 M NaCl at a bare electrode (position R in Figure 1) and a 35 μg SPCME (position S in Figure 1) after exposure to various concentrations of $[NaCl]^{-1/2}$ electrolyte solution for three different clay films. Time of exposure to the low concentration electrolyte solution was 8 minutes. The scan rate was 500 mV/s, and the flow rate was 5 mL/min.

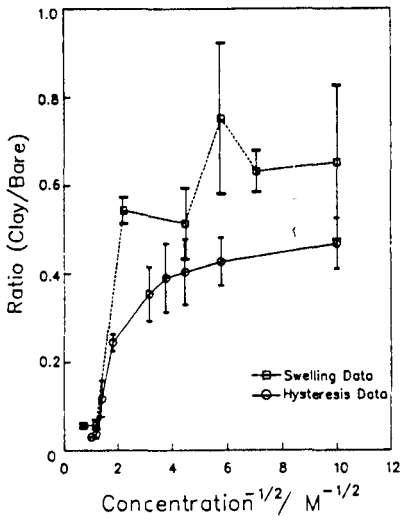

FIGURE 7. Plot of the ratio of the cathodic peak height for 2 mM $Fe(CN)_6^{3-}$ at a bare electrode and a 35 μg SPCME. Swelling data (-□-) are from previous work [10a] in which the ratio was measured in the salt solution indicated. The scan rate was 50 mV/s, and the equilibration time was 5 minutes. Hysteresis data (-○-) were obtained in the wall-tube cell. Measurements were made in 1 M NaCl. The bare electrode was in position R in Figure 1, and the SPCME was in position S in Figure 1. Time of exposure to the low concentration electrolyte solution was 8 minutes. The scan rate was 500 mV/s, and the flow rate was 5 mL/min.

front in the flow tubing. In order to eliminate problems with air bubbles adhering to the electrode surface, the jets were positioned face down and the electrodes face up in our system. This ensured that air bubbles were not trapped under the electrode. In addition, the jet was inserted slightly into the cell to prevent bubbles from adhering to the jet.

Break up of the Jet

When a lower electrolyte concentration solution was pumped into the higher concentration solution in the bulk volume wall-tube cell, the jet would not remain intact. By running the solution in at a higher flow rate (15 mL min^{-1}), this problem was rectified.

An experiment was conducted in an attempt to determine whether the jet disintegration was due to a difference in kinematic viscosity (which plays into the wall-tube equation) or to the development of a streaming potential. Two pairs of organic solvents were chosen. The first pair was water (kinematic viscosity = 1.005 cP cS^{-1}) run into 2% acetone (1.052 cP cS^{-1}). This pair had a difference in kinematic viscosity very close to the largest difference seen in the study (0.01 M NaCl (<1.005 cP cS^{-1}) run into 1 M NaCl (>1.056 cP cS^{-1})). The second pair was methanol (0.7547 cP cS^{-1}) run into ethanol (1.5203 cP cS^{-1}). This pair had a much larger difference than any seen in the NaCl system. Surprisingly, the jet remained intact better in the second system than in the first. In neither system, however, did the jet remain intact to the electrode surface. These results suggest that very slight differences in kinematic viscosity can cause the break up of the jet. It is important for people using large volume windowless electrochemical flow systems to note that such a difference could lead to problems [9].

While the breakup of the jet was solved by running the lower concentration electrolyte into the cell at a flow rate of 15 mL min^{-1}, this solution led to other problems. The high velocity of the flow stream required to maintain jet integrity could not be sustained for prolonged periods with the peristaltic pump. In addition, using this high flow rate caused problems with high background currents in the system. For these reasons, swelling was conducted by exposing the CME to a low electrolyte solution impinging on the jet at 15 mL min^{-1} while measurement of the swollen state was conducted in a high concentration electrolyte at a low flow rate. Because the high concentration electrolyte was the same as the initial solution and, hence, had the same kinematic viscosity, it did not require a high flow rate in order to impinge upon the jet. While this solved the problem of the pump, it led to an inherently different type of measurement than had been previously made.

CLAY-MODIFIED ELECTRODE STUDIES

In previous reports, the CME was first bathed in the electrolyte, transferred to a solution containing $Fe(CN)_6^{3-}$ and the electrolyte, and the measurement taken [10]. In this study, the CME was exposed to increasingly dilute concentrations of electrolyte, the solution changed to the most concentrated electrolyte solution (1 M NaCl which contained $Fe(CN)_6^{3-}$), and the measurement taken. There are two important differences between this method and the previous one. First, this system is measuring the swelling of the clay film in 1 M NaCl rather than in the electrolyte concentration which caused the swelling. We are measuring the swelling of the clay film which is irreversible with respect to 1 M NaCl rather than the simple swelling of the film. Second, in using a single clay film, one must ask if one is measuring the cumulative swelling of the film rather than the effect of a single process.

Prior to making any measurements in the system, it was important to verify that one was measuring the properties of the clay film. The film thickness, δ_f, for a 5 μg dry weight CME in its most swollen state (0.01 M NaCl) has been estimated to be 15 μm [5]. As calculated, the thickness of the boundary layer, δ_{bl}, in its most dilute state (0.01 M NaCl) was 824 μm. This shows that the film length is less than the boundary layer length. The depth of the diffusion layer in a quiescent solution is calculated to be 28 μm using a diffusion coefficient for $Fe(CN)_6^{3-}$ of 7×10^{-6} cm^2 s^{-1}. Since the diffusion coefficient is

expected to be less in the clay film, it can be assumed that this is the maximum thickness of our diffusion layer. Thus, $\delta_{dl} \leq \delta_f \ll \delta_{bl}$ and our measurements reflect the behavior of the clay film rather than changes in other parameters of the system.

Time of Swelling of the Clay Film

Since the clay film was exposed to dilute electrolyte for short periods of time, it was important to determine how long it took for the clay film to swell completely in response to the electrolyte. Figure 3 shows the ratio current as a function of time of exposure to electrolyte for several electrolyte concentrations. Each point on this curve reflects a new CME. Based on this data, we chose an 8 minute run time as optimum for all concentrations (see arrow, Figure 3) and used this time in all remaining studies. Notice that even after 10 minutes, the 1 M NaCl did not result in appreciable swelling of the clay film. This indicates that we can use the 1M NaCl for current measurements without having additional swelling occur.

Figure 4 shows multisweep cyclic voltammograms which were obtained for the two types of CME after exposure to 0.03 M NaCl. Notice the filling time before a steady state current is reached. This filling time has been modeled as the time for diffusional mixing of the two electrolyte solutions within the clay film [5]. The ODCME had a much shorter time for diffusional mixing than the SPCME. This is most likely due to the ODCME having a more randomly arranged clay film than the SPCME [4].

Irreversible Swelling of Clay Films

After determining the time needed to swell the clay film completely, the swelling of the clay in response to decreasing electrolyte concentrations was examined. Figure 5 shows the results obtained for three separate ODCMEs, while Figure 6 shows the results for three separate SPCMEs. These results were measured in a 1 M NaCl solution after exposure to the indicated electrolyte concentration. While there is variability present between the clay films, each film responds to the decreasing electrolyte concentration in a smooth manner. In previous work, a similar ratio, R, versus $[NaCl]^{-1/2}$ plots were obtained, where each data point was the average of three CMEs [10a]. Measurements in these plots had large error bars attached to each of the data points. This work shows that the error bars were due to the variability present between clay films; that is, it shows that a single clay film will swell in a smooth manner.

The dual tube-electrode cell gives data for the irreversible swelling of the clay film—the hysteresis of the clay film. Our previous work measured the direct swelling of the clay film. Figure 7 compares the results from these two types of measurements. The results are consistent with other work which has been done looking at the shrinking/swelling hysteresis of the clay [11]. The lower ratio which is seen during desorption of water can be attributed to a greater ordering of the water molecules present between the clay sheets and, hence, a more "crowded" pathway for the marker anion. It is this greater ordering which leads to hysteresis in the clay sheets.

CONCLUSIONS

In this study, the construction and use of a dual wall-tube electrode cell for CME studies are reported. In the system, the two working electrodes act independently and in a consistent manner. The system was used to measure the hysteresis of the clay film. The present system offers several advantages over the previously used method. It cuts the time needed to do an experiment from weeks to days, and it decreases the error present in the experiment both by allowing the bare and the modified measurements to be taken at the same time and by allowing a set of measurements to be made on a single clay film. While there is still considerable variability between the clay films, the wall-tube system allows us to see the nature of the response of a single clay film to an electrolyte. In previous studies, this data had been obscured by the error bars inherent to the method. In summary, the construction of a system which offers improvements in time, accuracy, and insight over the previously used system is reported.

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APPENDIX 3

WORK NOT PRESENTED IN DISSERTATION

Other projects that I worked on during the course of my time at Loyola University included investigations into the transport of nitrobenzene and cobalt sephulcate through a SWy-1 clay-modified electrode. The research that was conducted on these compounds was purely preliminary. However, because it laid the groundwork for the subsequent work of others, it is presented here, in brief.

Nitrobenzene is a compound that serves as an analog for compounds that are present as major pollutants in the environment. For this reason, its study is of interest. The electrochemical reaction of nitrobenzene is quite complex. For this reason, the scanning potentials were carefully selected to minimize the complexity of the reaction. A glassy carbon electrode was used because the reaction occurred at a potential to far negative to be accessed by a platinum electrode. Once the parameters for the study were determined, nitrobenzene was found to move easily through the clay film. The detection limit at the CME was 10^{-7} while at the bare electrode it was greater then 10^{-6}. These results were independent of the interlayer spacing within the clay film. This work showed that a small, aromatic compound will move easily through even a compressed clay bed (high electrolyte means low interlayer spacing). In addition, it showed that CME's can be used to model the movement of pollutants through clay beds.

Cobalt sephulcate ($Co(Sep)_3^{3+}$) has three biligand nitrogen rings attached to the central cobalt. Because the clay is negatively charged, it was postulated that the positively charged compound would move through the clay film at an accelerated rate. Similar results were seen for the positively charged $Ru(NH3)_6^{3+}$. In the studies with $Ru(NH3)_6^{3+}$, the compound was found to have a detection limit of 10^{-9}. Additionally,

the compound was found to move easily into and out of the clay film. In the $Co(Sep)_3^{3+}$ work, the compound moved easily through the clay film and was detected at very low concentrations. It would not, however, come out of the clay film. This irreversible binding to the clay film was postulated to be due to the aromatic nature of the compound. Work by other researchers verified this postulate.

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The dissertation is therefore accepted in partial fulfillment of the requirements for the degree of Ph.D. in Chemistry.

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